ENVIRONMENTAL CHEMISTRY
Tenth Edition
ANSWER MANUAL

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INTRODUCTION

This answer manual is provided as a teaching tool for faculty teaching environmental chemistry with the textbook *Environmental Chemistry*, Tenth Edition. The author welcomes input from users and suggestions for additional questions and problems. He may be contacted at the following e-mail address: manahans@missouri.edu

CONTENTS

Chapter 1
Environmental Chemistry and the Five Spheres of the Environment

1. Much of what is known about Earth's past history is based upon paleo-environmental studies. Doing some research on the internet, suggest what is meant by these studies. How can past climatic conditions, temperature, and atmospheric carbon dioxide levels be inferred going back hundreds of thousands of years based on ice cores and even millions of years based on fossils?

   Answer: Paleontology deals with ancient fossils, the nature of which reflects the climatic conditions under which they existed millions of years ago. Ice cores contain entrained air, the composition of which reflects climatic conditions from when the ice was formed as long as hundreds of thousands of years ago.

2. The idea of climate change caused by human activities appears to be relatively recent. However, it was proposed quite some time ago in a paper entitled "On the Influence of Carbonic Acid in the Air upon the Temperature of the Ground." When was this paper published and who was the author? What were his credentials and credibility?

   Answer: The article in question was published in 1896 in the *Philosophical Magazine and Journal of Science* by Svante Arrhenius, a Swedish Nobel-Prize-winning physicist and chemist with outstanding credentials and credibility.

3. The definition of environmental chemistry shown in Figure 1.4 could very well be illustrated with nitrogen oxides, NO and NO_2, emitted to the atmosphere. What would be the sources of these gaseous nitrogen oxides? Which secondary air pollutant would they form interacting with volatile hydrocarbons in the sunlight? Could acid rain result from these oxides and, if so, what would be the formula of the acid?

   Answer: The nitrogen oxides of most importance would come from pollutant combustion sources. Through photochemical reactions involving hydrocarbons the nitrogen oxides can cause the formation of photochemical smog. Acid rain in the form of HNO_3 can also be formed as a secondary air pollutant.

4. A number of reputable scientists now believe that the Holocene is ending and a new era has begun. What is the Holocene? What is the new era that may well be replacing it and how does it relate to material in this chapter? What are some of the environmental implications of this change?

   Answer: The Holocene is the relatively hospitable epoch under which humans have existed for the last approximately 10,000 years. It is being replaced by the Anthropocene in which human activities predominate in determining conditions on Earth.

5. In the late 1800s there was concern that within the nitrogen biogeochemical cycle, not enough of the atmosphere's inexhaustible store of nitrogen was being "fixed" to chemical forms that could be utilized by plants and that food shortages would result from a shortage of fixed nitrogen. What happened to change this situation? In what respect did this development save many lives and how did it also make possible the loss of millions of people in warfare after about 1900?

   Answer: The discovery of a synthetic chemical method to capture atmospheric nitrogen as ammonia, NH_3, enabled nitrogen fertilization of soil vastly increasing food productivity.

However, explosive organonitrogen compounds synthesized starting with ammonia killed millions of people in warfare.

6. In what respect is the term "solid earth" a misnomer? What are some specific events in the last decade that cast some doubt on "solid earth?" How did one of these events specifically impact the anthrosphere and perhaps change the course of future energy developments?

   Answer: The earth's outer shell rests on top of a layer of hot, molten rock. Earth is prone to earthquakes and volcanoes. The Fukushima Daiichi nuclear disaster that resulted from a massive earthquake and tsunami on the coast of Japan has essentially shut down Japan's once-thriving nuclear energy development.

7. In what important, fundamental respect does the phosphorus cycle differ from the carbon, oxygen, and nitrogen cycles?

   Answer: The phosphorus cycle does not have an atmospheric component as do the other cycles mentioned.

8. Most people are aware that atmospheric carbon dioxide contributes to global warming and climate change. In what respect, however, is the atmosphere's carbon dioxide part of Earth's natural capital, that is, where would we be without it? What crucial natural phenomenon causes a slight, but perceptible change in atmospheric carbon dioxide levels over the course of a year?

   Answer: In addition to keeping Earth's temperature at a livable level, atmospheric carbon dioxide provides the carbon for the photosynthetic organisms that provide food for essentially all organisms. Especially in the Northern Hemisphere, atmospheric carbon dioxide levels go through an annual cycle as the result of photosynthesis.

9. Figure 1.4 illustrates the definition of environmental chemistry in terms of a common pollutant. What command and control regulations have been implemented in limiting this source of pollution? What "end-of-pipe" measures have been used? Suggest how the practices of green chemistry might serve as alternatives to these measures?

   Answer: Command and control regulations have been put in place to limit allowable emissions of sulfur dioxide. "End-of-pipe" control measures have concentrated upon removing pollutants from the waste stream after they have been produced, such as by scrubbing sulfur dioxide from a coal-fired powerplant stack. The practice of green chemistry seeks to prevent pollutants from being produced.

10. As it applies to environmental processes and pollution, the term "sink" is sometimes used. With some search on the internet, explain what is meant by a sink as it applies to environmental pollution. In what sense is Earth's ability to act as a sink part of its natural capital? Explain.

    Answer: A sink is the final resting place of a pollutant. The geosphere's ability to absorb and degrade wastes placed in it is an important part of its natural capital.

11. In dealing with pollution and the potential for pollution, three approaches are pollution prevention, end-of-pipe measures, and remediation. What do these terms mean in terms of pollution control? Which is the most desirable, and which is the least? Explain.

    Answer: In descending order of desirability these means of pollution control are (1) prevention of the production of pollutants, (2) end-of-pipe measures that remove pollutants from waste streams before they can be discharged, and (3) remediation by treating or removing pollutants after they have been discharged, usually to the geosphere.

12. With respect to increased production of corn to provide fuel ethanol, it is stated in this

chapter that, "Increased demand for fertilizer in the form of chemically combined nitrogen means that more ammonia is synthesized using atmospheric nitrogen and impacting the nitrogen cycle." With respect to which resource of Earth's capital is the synthetic production of nitrogen fertilizer as it is now done a problem, and in respect to which resource is it **not** a problem. Explain.

Answer: Currently the hydrogen required to make ammonia is extracted from methane, a depleting resource of natural capital, in a process that discharges carbon dioxide to the atmosphere. Elemental nitrogen is also used, but the atmosphere has an inexhaustible store of that resource.

Chapter 2
The Hydrosphere and Water Chemistry

1. Alkalinity is determined by titration with standard acid. The alkalinity is often expressed as mg/L of $CaCO_3$. If V_p mL of acid of normality N are required to titrate V_s mL of sample to the phenolphthalein endpoint, what is the formula for the phenolphthalein alkalinity as mg/L of $CaCO_3$?

   Answer: $(V_p \times N)/V_S$

2. Exactly 100 pounds of cane sugar (dextrose), $C_{12}H_{22}O_{11}$, were accidentally discharged into a small stream saturated with oxygen from the air at 25°C. How many liters of this water could be contaminated to the extent of removing all the dissolved oxygen by biodegradation?

   Answer: The calculation is the following, where Dx is dextrose

$$4.54 \times 10^4 \text{ g Dx} \times \frac{1 \text{ mol Dx}}{342 \text{ g Dx}} \times \frac{12 \text{ mol } O_2}{1 \text{ mol Dx}} \times \frac{3.20 \times 10^4 \text{ mg } O_2}{1 \text{ mol } O_2} \times \frac{1 \text{ L}}{8.32 \text{ mg } O_2} = 6.13 \times 10^6 \text{ L}$$

3. Water with an alkalinity of 2.00×10^{-3} equivalents/liter has a pH of 7.00. Calculate $[CO_2]$, $[HCO_3^-]$, $[CO_3^{2-}]$, and $[OH^-]$.

   Answer: At pH = 7.00, the alkalinity is due to the $[HCO_3^-]$ and hence $[HCO_3^-] = 2.00 \times 10^{-3}$ eq/l. The $[OH^-] = 1.00 \times 10^{-7}$ eq/l and the $[CO_2]$ can be calculated by substituting the values of $[HCO_3^-]$ and $[H^+]$ in the k_{a1} expression and then solving for $[CO_2]$. The $[CO_3^{2-}]$ can be calculated by substituting the values of $[HCO_3^-]$ and $[H^+]$ in the k_{a1} expression:

$$K_{a1} = 4.45 \times 10^{-7} = \frac{[1.00 \times 10^{-7}] \times [2.00 \times 10^{-3}]}{[CO_2]}$$
$$[CO_2] = 4.49 \times 10^{-4}$$

$$K_{a2} = 4.69 \times 10^{-11} = \frac{[1.00 \times 10^{-7}] \times [CO_3^{2-}]}{2.00 \times 10^{-3}}$$
$$[CO_3^{2-}] = 9.38 \times 10^{-7}$$

4. Through the photosynthetic activity of algae, the pH of the water in Problem 3 was changed to 10.00. Calculate all the preceding concentrations and the weight of biomass, $\{CH_2O\}$, produced. Assume no input of atmospheric CO_2.

   Answer: Since the pH has changed to 10.00, $[H^+] = 1 \times 10^{-10}$ and $[OH^-] = 1.00 \times 10^{-4}$ The alkalinity is calculated by the formula:

   $[alk] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] = 2.00 \times 10^{-3}$. The values of $[CO_3^{2-}]$ and $[HCO_3^-]$ are related by the formula

$$[CO_3^{2-}] = \frac{K_{a2} \times [HCO_3^-]}{[H^+]} = 0.469[HCO_3^-]$$

   Substitute this expression for $[CO_3^{2-}]$ into the alkalinity formula in which $[OH^-] = 1.00 \times 10^{-4}$ to solve for $[HCO_3^-] = 9.8 \times 10^{-4}$. The value of $[CO_3^{2-}]$ can be calculated by the

K_{a2} formula giving $[CO_3^{2-}] = 4.60 \times 10^{-4}$.

The amount of biomass produced can be calculated by finding out the difference between the amounts of total dissolved inorganic carbon at the 2 pH values as follows $[C] = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$

At pH= 7.00, [C] = 2.45×10^{-3} and at pH = 10.00 [C] = 1.44×10^{-3}. $[C]_{pH7} \times 1L - [C]_{pH10}$ x $1L = 1.01 \times 10^{-3}$. Since the molar mass of biomass $\{CH_2O\}$ = 30 g/mol, this number can be converted to the amount of biomass produced by the following calculation:

$$1.01\times10^{-3}\frac{\text{mol}}{\text{L}}\times30\frac{\text{g}}{\text{mol}} = 3.03\times10^{-2}\frac{\text{g}}{\text{L}} = 30.3\frac{\text{mg}}{\text{L}}$$

5. Calcium chloride is quite soluble, whereas the solubility product of calcium fluoride, CaF_2, is only 3.9×10^{-11}. A waste stream of 1.00×10^{-3} M HCl is injected into a formation of limestone, $CaCO_3$, where it comes into equilibrium. Give the chemical reaction that occurs and calculate the hardness and alkalinity of the water at equilibrium. Do the same for a waste stream of 1.00×10^{-3} M HF.

   Answer: The reaction with HCl is:
   $CaCO_3 + HCl \rightarrow Ca^{2+} + Cl^- + HCO_3^-$, the hardness = $[Ca^{2+}] = 1.00 \times 10^{-3}$ and the alkalinity = $[HCO_3^-] = 1.00 \times 10^{-3}$
   In the presence of the HF the reaction becomes:
   $2CaCO_3 + 2HF \rightarrow CaF_2 + 2HCO_3^- + Ca^{2+}$
   Based upon the stoichiometry of this reaction $[HCO_3^-] = 1.00 \times 10^{-3}$ = alkalinity and $[Ca^{2+}] = 5.00 \times 10^{-4}$ = hardness. A slightly higher value of $[Ca^{2+}]$ and hardness results from the dissociation of CaF_2.

6. For a solution having 1.00×10^{-3} equivalents/liter total alkalinity (contributions from HCO_3^-, CO_3^{2-}, and OH^-) at $[H^+] = 4.69 \times 10^{-11}$, what is the percentage contribution to alkalinity from CO_3^{2-}? 2.62+2.62+2.62+2.13

   Answer: Alkalinity = $[HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$
   Since $[H^+] = 4.69 \times 10^{-11}$, $[OH^-] = 2.13 \times 10^{-4}$. Since $[H^+] = 4.69 \times 10^{-11}$, from the expression for K_{a1}, $[HCO_3^-] = [CO_3^{2-}]$. Thus
   Alkalinity = $1.00 \times 10^{-3} = [HCO_3^-] + 2[HCO_3^-] + 2.13 \times 10^{-4}$
   $[HCO_3^-] = 2.62 \times 10^{-4}$ and $[CO_3^{2-}] = 2.62 \times 10^{-4}$
   The % contribution of the $CO_3^{2-} = (5.24 \times 10^{-4}/1.00 \times 10^{-3}) \times 100\% = 52.4\%$

7. A wastewater disposal well for carrying various wastes at different times is drilled into a formation of limestone ($CaCO_3$), and the wastewater has time to come to complete equilibrium with the calcium carbonate before leaving the formation through an underground aquifer. Of the following components in the wastewater, the one that would not cause an increase in alkalinity due either to the component itself or to its reaction with limestone, is (a) NaOH, (b) CO_2, (c) HF, (d) HCl, (e) all of the preceding would cause an increase in alkalinity.

   Answer: (e) All of the preceding would cause an increase in alkalinity

8. Calculate the ratio $[PbT^-]/[HT^{2-}]$ for NTA in equilibrium with $PbCO_3$ in a medium having $[HCO_3^-] = 3.00 \times 10^{-3}$ M.

   Answer: The reaction is $PbCO_3(s) + HT^{2-} \leftrightarrow PbT^- + HCO_3^-$ and, designating the equilibrium constant of this reaction as K, the following applies:

$$\frac{[PbT^-]}{[HT^{2-}]} = \frac{K}{[HCO_3^-]} = \frac{4.06 \times 10^{-2}}{3.00 \times 10^{-3}} = 13.5$$

9. If the medium in Problem 8 contained excess calcium such that the concentration of uncomplexed calcium, $[Ca^{2+}]$, were 5.00×10^{-3} M, what would be the ratio $[PbT^-]/[CaT^-]$ at pH 7?

   Answer: The reaction is $PbCO_3(s) + CaT^- + HT^2 \leftrightarrow Ca^{2+} + HCO_3^- + PbT^-$ for which the equilibrium constant may be designated K", which has a value of 5.24, and the following applies when $[HCO_3^-] = 3.00 \times 10^{-3}$ M and $[Ca^{2+}] = 5.00 \times 10^{-3}$ M and the ratio is 0.0349:

$$\frac{[PbT^-]}{[CaT^-]} = \frac{[H^+]\,K''}{[Ca^{2+}][HCO_3^-]} = 0.0349$$

10. A wastewater stream containing 1.00×10^{-3} M disodium NTA, Na_2HT, as the only solute is injected into a limestone ($CaCO_3$) formation through a waste disposal well. After going through this aquifer for some distance and reaching equilibrium, the water is sampled through a sampling well. What is the reaction between NTA species and $CaCO_3$? What is the equilibrium constant for the reaction? What are the equilibrium concentrations of CaT^-, HCO_3^-, and HT^{2-}? (The appropriate constants may be looked up in this chapter.)

    Answer: The reaction is $CaCO_3(s) + HT^{2-} \leftrightarrow CaT^- + HCO_3^-$ from which the following may be calculated:

$$K = \frac{[CaT^-]\,[HCO_3^-]}{[HT^{2-}]} = \frac{K_{sp} \times K'}{K_{a2}} = \frac{4.47 \times 10^{-9} \times 7.75 \times 10^{-3}}{4.69 \times 10^{-11}} = 0.739$$

$$[CaT^-] = [HCO_3^-] = 1.00 \times 10^{-3} \text{ and } [HT^{2-}] = 1.35 \times 10^{-6}$$

11. If the wastewater stream in Problem 10 were 0.100 M in NTA and contained other solutes that exerted a buffering action such that the final pH were 9.00, what would be the equilibrium value of HT^{2-} concentration in moles/liter?

    Answer: At equilibrium $[CaT^-] = [HCO_3^-]$ and $[HT^{2-}] = 0.100 - [CaT^-]$

$$K = 0.739 = \frac{[CaT^-][CaT^-]}{0.100 - [CaT^-]} \text{ so } = [CaT^-] = 0.0892 \text{ and } [HT^{2-}] = 0.0108$$

12. Exactly 1.00×10^{-3} mole of $CaCl_2$, 0.100 mole of NaOH, and 0.100 mole of Na_3T were mixed and diluted to 1.00 liter. What was the concentration of Ca^{2+} in the resulting mixture?

    Answer: Under these conditions all the Ca is bound to the NTA and excess NTA is present as T^{3-} so that:

$$[CaT^-] = 1.00 \times 10^{-3} \qquad [T^{3-}] = 0.100 - [CaT^-] = 0.099$$

$$K_f = \frac{[CaT^-]}{[Ca^{2+}][T^{3-}]} = 1.48 \times 10^8$$

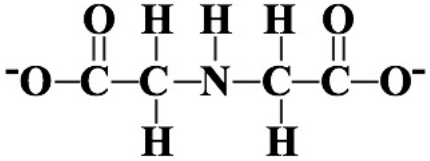
$$[Ca^{2+}] = 6.83 \times 10^{-11}$$

13. How does chelation influence corrosion?

    Answer: Chelation tends to increase corrosion by shifting redox potentials toward

oxidation and by dissolving protective metal oxide coatings.

14. The following ligand has more than one site for binding to a metal ion. How many such sites does it have?



Answer: There are three binding sites, one to each of the two carboxylate groups and one to the N atom

15. If a solution containing initially 25 mg/L trisodium NTA is allowed to come to equilibrium with solid $PbCO_3$ at pH 8.50 in a medium that contains 1.76×10^{-3} M HCO_3^- at equilibrium, what is the value of the ratio of the concentration of NTA bound with lead to the concentration of unbound NTA, $[PbT^-]/[HT^{2-}]$?

Answer: The reaction is $PbCO_3(s) + HT^{2-} \leftrightarrow PbT^- + HCO_3^-$ for which K = 0.046 and from which the following may be calculated:

$$\frac{[PbT^-]}{[HT^{2-}]} = \frac{K}{[HCO_3^-]} = \frac{4.06 \times 10^{-2}}{1.76 \times 10^{-3}} = 23.1$$

16. After a low concentration of NTA has equilibrated with $PbCO_3$ at pH 7.00 in a medium having $[HCO_3^-] = 7.50 \times 10^{-4}$ M, what is the ratio of $[PbT^-]/[HT^{2-}]$?

Answer: 54.1

17. What detrimental effect may dissolved chelating agents have upon conventional biological waste treatment?

Answer: The presence of chelating agents in the sewage may prevent heavy metals from being removed by the sewage sludge (biosolids)

18. Why is chelating agent usually added to artificial algal growth media?

Answer: To keep micronutrient iron in solution

19. What common complex compound of magnesium is essential to certain life processes?

Answer: Chlorophyll, which conducts photosynthesis

20. What is always the ultimate product of polyphosphate hydrolysis?

Answer: Orthophosphate, usually as $H_2PO_4^-$ or HPO_4^{2-}

21. A solution containing initially 1.00×10^{-5} M CaT^- is brought to equilibrium with solid $PbCO_3$. At equilibrium, pH = 7.00, $[Ca^{2+}] = 1.50 \times 10^{-3}$ M, and $[HCO_3^-] = 1.10 \times 10^{-3}$ M. At equilibrium, what is the fraction of total NTA in solution as PbT^-?

Answer: The reaction is $PbCO_3(s) + CaT^- + H^+ \leftrightarrow Ca^{2+} + HCO_3^- + PbT^-$ for which the equilibrium constant may be designated K", which has a value of 5.24, and the following applies at pH 7.00 when $[HCO_3^-] = 1.10 \times 10^{-3}$ M and $[Ca^{2+}] = 1.50 \times 10^{-3}$ M.:

$$\text{Fraction of NTA as } PbT^- = \frac{[PbT^-]}{[CaT^-] + [PbT^-]} = \frac{[PbT^-]/[CaT^-]}{[CaT^-]/[CaT^-] + [PbT^-]/[CaT^-]} = 0.318$$

$$= \frac{0.318}{1.000 + 0.318} = 0.241$$

22. What is the fraction of NTA present as HT^{2-} after HT^{2-} has been brought to equilibrium with solid $PbCO_3$ at pH 7.00 in a medium in which $[HCO_3^-] = 1.25 \times 10^{-3}$ M.

Answer: The reaction is $PbCO_3(s) + HT^{2-} \leftrightarrow PbT^- + HCO_3^-$ for which K = 0.046 and from which the following may be calculated:

$$\frac{[PbT^-]}{[HT^{2-}]} = \frac{K}{[HCO_3^-]} = \frac{4.06 \times 10^{-2}}{1.25 \times 10^{-3}} = 32.5$$

$$\text{Fraction of NTA as } HT^{2-} = \frac{[HT^{2-}]}{[PbT^-] + [HT^{2-}]} = \frac{[HT^{2-}]/[HT^{2-}]}{[PbT^-]/[HT^{2-}] + [HT^{2--}]/[HT^{2-}]}$$

$$= \frac{1.00}{32.5 + 1.00} = 0.030$$

23. Describe ways in which measures taken to alleviate water supply and flooding problems might actually aggravate such problems.

Answer: Diversion of water to municipal and irrigation uses has resulted in depletion of water sources and degradation of water quality, such as by adding salinity. Construction of dikes along rivers to alleviate flooding has resulted in catastrophic flooding when these structures fail during extreme flooding events.

24. The study of water is known as _____, _____, _____ is the branch of the science dealing with the characteristics of fresh water, and the science that deals with about 97% of all Earth's water is called _____.

Answer: Hydrology, limnology, and oceanography, respectively.

25. Consider the hydrologic cycle in Figure 2.1. List or discuss the kinds or classes of environmental chemistry that might apply to each major part of this cycle.

Answer: Oceanography applies to water in the ocean, by far the largest amount in the cycle; atmospheric chemistry interacts with water in the atmosphere, such as in formation of condensation nuclei around which cloud droplets form; limnology applies to fresh water in streams and lakes; chemistry of the geosphere interacts with aquatic chemistry in groundwater; water in soil is very much involved with soil chemistry.

26. Consider the unique and important properties of water. What molecular or bonding characteristics of the water molecules are largely responsible for these properties. List or describe one of each of the following unique properties of water related to (a) thermal characteristics, (b) transmission of light, (c) surface tension, (d) solvent properties.

Answer: (a) The high heat capacity and high heats of vaporization and fusion of water are due largely to its hydrogen bonding tendencies; (b) the transmission of light is the result of the lack of chromophores that absorb visible light in the water molecule; (c) the high surface tension is largely due to the strong bonding of water molecules with each other; and (d) the solvent properties of water, such as the high solubility of ionic solutes in it, are due largely to the polar nature of the water molecule and its hydrogen bonding capability.

27. Discuss how thermal stratification of a body of water may affect its chemistry.

Answer: (a) The high heat capacity and high heats of vaporization and fusion of water are due largely to its hydrogen bonding tendencies; (b) the transmission of light is the result of the lack of chromophores that absorb visible light in the water molecule; (c) the

high surface tension is largely due to the strong bonding of water molecules with each other; and (d) the solvent properties of water, such as the high solubility of ionic solutes in it, are due largely to the polar nature of the water molecule and its hydrogen bonding capability.

28. Relate aquatic life to aquatic chemistry. In so doing, consider the following: autotrophic organisms, producers, heterotrophic organisms, decomposers, eutrophication, dissolved oxygen, biochemical oxygen demand.

Answer: As several examples, photosynthetic autotrophic organisms are producers that generate biomass that provides the base of the aquatic food web; producers require adequate nutrients to generate biomass, but if the nutrients are excessive, eutrophication may result; too much biomass in water can result in excessive biochemical oxygen demand in water with depletion of dissolved oxygen.

29. Assuming levels of atmospheric CO_2 are 400 ppm CO_2, what is the pH of rainwater due to the presence of carbon dioxide? Some estimates are for atmospheric carbon dioxide levels to double in the future. What would be the pH of rainwater if this happens?

Answer: As noted in Section 3.7, the value of $[CO_2(aq)]$ in water at 25°C in equilibrium with air that is 400 ppm CO_2 is 1.309×10^{-5} M. In pure rainwater, the carbon dioxide dissociates partially in water to produce equal concentrations of H^+ and HCO_3^- and from the K_{a1} expression for CO_2, $[H^+] = 2.41 \times 10^{-6}$ and pH = 5.61. Doubling atmospheric CO_2 levels would double the concentration of CO_2 in rainwater to 2.618×10^{-5} M and, as shown in Section 2.7, this gives $[H^+] = 3.41 \times 10^{-6}$ and pH = 5.47.

30. Assume a sewage treatment plant processing 1 million liters of wastewater per day containing 200 mg/L of degradable biomass, $\{CH_2O\}$. Calculate the volume of dry air at 25°C that must be pumped into the wastewater per day to provide the oxygen required to degrade the biomass (Reaction 2.6.1).

Answer: The reaction is $\{CH_2O\} + O_2 \rightarrow CO_2 + H_2O$. The amount of biomass present in the 1 million liters of water is 2.00×10^8 mg = 2.00×10^5 g. The moles of O_2 required to react with this biomass are

$$2.00 \times 10^5 \text{ g } \{CH_2O\} \times \frac{1 \text{ mol } \{CH_2O\}}{30 \text{ g } \{CH_2O\}} \times \frac{1 \text{ mol } O_2}{1 \text{ mol } \{CH_2O\}} = 6.67 \times 10^3 \text{ mol } O_2$$

Since only 20.95% of dry air is O_2, the moles of air needed to supply this $O_2 = 3.18 \times 10^4$ mole. The volume of this amount of air at 25°C and 1 atm pressure can be calculated by the ideal gas law, PV = nRT, where R = 0.0821 L atm mol^{-1} giving 7.78×10^5 L of air. Only a fraction of the oxygen in the air is actually transferred into the sewage, so significantly more air would need to be pumped to supply the oxygen required.

31. Anoxic bacteria growing in a lake sediment produced equal molar amounts of carbon dioxide and carbon monoxide according to the biochemical reaction $2\{CH_2O\} \rightarrow CO_2 + CH_4$, so that the water in the lake was saturated with both CO_2 gas and CH_4 gas. In units of mol × L^{-1} × atm^{-1} the Henry's law constant for CO_2 is 3.38×10^{-2} and that of CH_4 has a value of 1.34×10^{-3}. At the depth at which the gas was being evolved, the total pressure was 1.10 atm and the temperature was 25°C, so the vapor pressure of water was 0.0313 atm. Calculate the concentrations of dissolved CO_2 and dissolved CH_4.

Answer: Since equimolar amounts of CO_2 and CH_4 are evolved, the mole fraction of each gas = 0.500. The partial pressure of each gas = 0.500 × 1.10 = 0.550 atm. The corrected pressure of each gas = 0.550 - 0.0313 = 0.519. Using Henry's law, $[CO_2]$ =

$0.519\ \text{atm} \times 3.38 \times 10^{-2}\ \text{mol} \times \text{L}^{-1} \times \text{atm}^{-1} = 1.75 \times 10^{-2}\ \text{M}$ and $[CH_4] = 6.95 \times 10^{-4}\ \text{M}$.

Chapter 3
Oxidation/Reduction In Aquatic Chemistry

1. The acid-base reaction for the dissociation of acetic acid is

   $HOAc + H_2O \rightarrow H_3O^+ + OAc^-$

   with $K_a = 1.75 \times 10^{-5}$. Break this reaction down into two half-reactions involving H^+ ion. Break down the redox reaction

   $Fe^{2+} + H^+ \rightarrow Fe^{3+} + 1/2H_2$

   into two half-reactions involving the electron. Discuss the analogies between the acid-base and redox processes.

   Answer: The first reaction may be regarded as the sum of two half-reactions involving the loss and gain of H^+ ion:

   $HOAc \rightarrow H^+ + OAc^-$

   $H_2O + H^+ \rightarrow H_3O^+$

   The second reaction may be regarded as the sum of two half-reactions involving the loss and gain of an electron:

   $Fe^{2+} \rightarrow Fe^{3+} + e^-$

   $H^+ + e^- \rightarrow {}^1/_2H_2$

   Both of these types of reactions involve the transfer of a species (H^+ in case of acids and bases, e^- in redox), both types of reactions have a donor and an acceptor species involved, and both can be divided into half reactions which when added together will give the original reaction.

2. Assuming a bicarbonate ion concentration $[HCO_3^-]$ of 1.00×10^{-3} M and a value of 3.5×10^{-11} for the solubility product of $FeCO_3$, what would you expect to be the stable iron species at pH 9.5 and pE -8.0, as shown in Figure 3.4?

   Answer: Figure 3.4 shows the predominance of iron species in pE/pH regions where the only ion that would form precipitates with iron species is the hydroxide ion, OH^-. At pH 9.5 and pE -8.0, the predominant iron species in such a system as shown by the diagram would be solid $Fe(OH)_2$. As discussed in Section 3.11, the solubility relationship for $Fe(OH)_2$ is

   $Fe(OH)_2(s) + 2H^+ \leftrightarrow Fe^{2+} + 2H_2O$

   $$K_{sp} = \frac{[Fe^{2+}]}{[H^+]^2} = 8.0 \times 10^{12}$$

   from which at pH 9.5 the concentration of in Fe^{2+} in the system would be given by the following:

   $[Fe^{2+}] = K_{sp}[H^+]^2 = 8.0 \times 10^{12} \times (10^{-9.5})^2 = 8.0 \times 10^{-7}$

   However, in the presence of HCO_3^-, it is possible that $FeCO_3(s)$ would be less soluble than $Fe(OH)_2$. When $[HCO_3^-] = 1.00 \times 10^{-3}$ at pH 9.5, the expression for the acid dissociation constant of HCO_3^-, K_{a2}, gives the following:

$$[CO_3^{2-}] = \frac{[HCO_3^-]}{[H^+]} K_{a2} = \frac{1.00 \times 10^{-3}}{3.16 \times 10^{-10}} \times 4.69 \times 10^{-11} = 1.48 \times 10^{-4}$$

Substituting this value into the expression for the solubility product of $FeCO_3$ gives:

$[Fe^{2+}] = K_{sp}/[CO_3^{2-}] = 3.5 \times 10^{-11}/1.48 \times 10^{-4} = 2.36 \times 10^{-7}$

Since this value of $[Fe^{2+}]$ is lower than that calculated from the solubility of $Fe(OH)_2$ under the same conditions, it is likely that $FeCO_3(s)$ would be the predominant iron species.

3. Assuming that the partial pressure of oxygen in water is that of atmospheric O_2, 0.21 atm, rather than the 1.00 atm assumed in deriving Equation 3.9.5, derive an equation describing the oxidizing pE limit of water as a function of pH.

   Answer: $pE = 20.75 + {}^1/_4 \log P_{O_2} - pH$, substitute $P_{O_2} = 0.21$ atm to get $pE = 20.58 - pH$.

4. Plot log P_{O_2} as a function of pE at pH 7.00.

   Answer: At pH = 7.00, $pE = 13.75 + {}^1/_4 \log P_{O_2}$, this equation can be used to plot log P_{O_2} as a function of pE.

5. Calculate the pressure of oxygen for a system in equilibrium in which $[NH_4^+] = [NO_3^-]$ at pH 7.00.

   Answer: From table 3.1, half reaction #5 pE^0 (at pH 7.00) = 6.15 and applying the Nernst equation to half-reaction #1 in Table 3.1 gives the following:

   $pE = 13.75 + {}^1/_4 \log P_{O_2}$, since pE = 6.15, $P_{O_2} = 3.98 \times 10^{-31}$

6. Calculate the values of $[Fe^{3+}]$, pE, and pH at the point in Figure 3.4 where Fe^{2+} at a concentration of 1.00×10^{-5} M, $Fe(OH)_2$, and $Fe(OH)_3$ are all in equilibrium.

   Answer: Examination of Figure 3.4 shows that this condition exists only at the point where the boundary line between the region where Fe^{2+} predominates and that where $Fe(OH)_3$ is the predominant species ($pE = 22.2 - 3\ pH$) intersects the boundary line between $Fe(OH)_3$ and $Fe(OH)_2$ ($pE = 4.3 - pH$). Solving these two equations yield pE = -4.65 and pH = 8.95. Substituting $[H^+]$ into the solubility product expression for $[Fe^{3+}]$, below, gives $[Fe^{3+}] = 1.28 \times 10^{-23}$

$$K'_{sp} = \frac{[Fe^{3+}]}{[H^+]^3} = 9.1 \times 10^3$$

7. What is the pE value in a solution in equilibrium with air (21% O_2 by volume) at pH 6.00?

   Answer: The pertinent half-reaction is ${}^1/_4 O_2 + H^+ + e^- \leftrightarrow {}^1/_2 H_2O$ $pE^0 = 20.75$

   The partial pressure of air is 0.21 atm and solving the Nernst equation below for which $pE^0 = 20.75$ gives a pE value of 14.6.

$$pE = pE^0 + \log(P_{O_2}^{1/4}[H^+])$$

8. What is the pE value at the point on the Fe^{2+}–$Fe(OH)_3$ boundary line (see Figure 3.4) in a solution with a soluble iron concentration of 1.00×10^{-4} M at pH 6.00?

   Answer: The equation that pertains is given below in which the K_{sp} is that of $Fe(OH)_3$ with a value of 9.1×10^3, the solution of which gives pE = 3.16.

$$pE = 13.2 + \log \frac{K_{sp}'[H^+]^3}{[Fe^{2+}]}$$

9. What is the pE value in an acid mine water sample having $[Fe^{3+}] = 7.03 \times 10^{-3}$ M and $[Fe^{2+}] = 3.71 \times 10^{-4}$ M?

   Answer: Substituting the appropriate concentration values into Nernst equation below gives pE = 14.5.

$$pE = 13.2 + \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

10. At pH 6.00 and pE 2.58, what is the concentration of Fe^{2+} in equilibrium with $Fe(OH)_3(s)$?

    Answer: Solving the equation below that pertains to the boundary between Fe^{2+} and $Fe(OH)_3$ gives = $[Fe^{2+}] = 3.79 \times 10^{-4}$ M.

$$pE = 13.2 + \log \frac{K_{sp}'[H^+]^3}{[Fe^{2+}]}$$

11. What is the calculated value of the partial pressure of O_2 in acid mine water of pH 2.00, in which $[Fe^{3+}] = [Fe^{2+}]$?

    Answer: Since $[Fe^{3+}] = [Fe^{2+}]$, pE = 13.2 and solving the Nernst equation below for which $pE^0 = 20.75$ gives $P_{O_2} = 6.31 \times 10^{-23}$.

$$pE = pE^0 + \log(P_{O_2}^{1/4}[H^+])$$

12. What is the major advantage of expressing redox reactions and half-reactions in terms of exactly one electron-mole?

    Answer: To provide a common basis for comparison, specifically, the transfer of 1 mole of electrons.

13. Why are pE values that are determined by reading the potential of a platinum electrode versus a reference electrode generally not very meaningful?

    Answer: The electrode often does not behave reversibly so that it does not accurately reflect the comparative activities of the oxidized and reduced species in solution

14. What determines the oxidizing and reducing limits, respectively, for the thermodynamic stability of water?

    Answer: The oxidizing limit is defined by the oxidation of H_2O to give O_2 gas and the reducing limit is defined by the reduction of H_2O to give H_2 gas.

15. How would you expect pE to vary with depth in a stratified lake?

    Answer: As the depth increases, the level of dissolved O_2 goes down so that pE can approach levels near the reducing limit of stability as shown by the lower dashed diagonal line in Figure 3.4.

16. Upon what half-reaction is the rigorous definition of pE based?

    Answer: The half-reaction is $2H^+ (aq) + 2e^- \leftrightarrow H_2(g)$ for which E^0 is defined as exactly 0.00 volts and $pE^0 = 0.00$.

17. Analysis of water in a sediment sample at equilibrium at pH 7.00 showed $[SO_4^{2-}] = 2.00 \times 10^{-5}$ M and a partial pressure of H_2S of 0.100 atm. Show with appropriate calculations if methane, CH_4, would be expected in the sediment.

Answer: The pertinent half-reactions are the following:

$^1/_8SO_4^{2-} + {}^5/_4H^+(W) + e^- \leftrightarrow {}^1/_8H_2S(g) + {}^1/_2H_2O \quad pE^0(W) = -3.50$

$^1/_8CO_2 + H^+(W) + e^- \leftrightarrow {}^1/_8CH_4 + {}^1/_4H_2O \quad pE^0(W) = -4.13$

The Nernst equations pertaining to these half-reactions are below in which the $[H^+]$ terms drop out because of the use of $pE^0(W)$ values that apply at a fixed pH of 7.00:

$$pE = -3.50 + \log \frac{[SO_4^{2-}]}{P_{H_2S}^{1/8}} \qquad pE = -4.13 + \log \frac{P_{CO_2}^{1/8}}{P_{CH_4}^{1/8}}$$

Using the Nernst equation that applies to the SO_4^{2-}/H_2S system and inserting the value of $[SO_4^{2-}] = 2.00 \times 10^{-5}$ and 0.100 for the pressure of H_2S gives pE = -4.57. Substituting this value for pE into the second Nernst equation above gives a value of -0.44 for the log term in that equation showing that the partial pressure of CO_2 is less than that of CH_4 so that CH_4 would be present at significant levels in the sediment.

18. Choose the correct answer of the following, explain why it is true, and explain why the other choices are untrue: (A) High pE is associated with species such as CH_4, NH_4^+, and Fe^{2+}: (B) low pE is associated with species such as CO_2, O_2, and NO_3^-; (C) values of pE in bodies of water range from about 1×10^{-7} to about 1×10^7; (D) pE is a number, but cannot be related to anything real, such as is the case with pH; (E) pE uses convenient numbers to express electron activity over many orders of magnitude.

    Answer: E

19. Match each of the following from the lettered list to the reaction that corresponds to it from the numbered list below:

    (A) For 1 electron-mole

    (B) Reaction for standard electrode

    (C) At upper pE limit of water

    (D) Formation of a pollutant when anoxic water is brought to the surface

    (1) $Fe(H_2O)_6^{2+} \leftrightarrow e^- + Fe(OH)_3\,(s) + 3H_2O + 3H^+$

    (2) $H_2 \leftrightarrow 2H^+ + 2e^-$

    (3) $1/8NH_4^+ + 1/4O_2 \leftrightarrow 1/8NO_3^- + 1/4H^+ + 1/8H_2O$

    (4) $2H_2O \leftrightarrow O_2 + 4H+ + 4e^-$

    Answer: (A)-(3), (B)-(2), (C)-(4), (D)-(1)

20. Of the following, the true statement regarding oxidation-reduction reactions and phenomena in natural water systems is (A) at a pE higher than the oxidizing limit of stability water decomposes to evolve H_2, (B) the production of CH_4 at a very low pE is caused to occur by the action of bacteria, (C) In the pE-pH diagram for iron, the region of greatest area is occupied by solid $Fe(OH)_2$, (D) It is easy to accurately measure pE of water with a platinum electrode, (F) There are no pE/pH limits for the regions of stability of H_2O.

    Answer: B

Chapter 4
Phase Interactions in Aquatic Chemistry

1. A sediment sample was taken from a lignite strip-mine pit containing highly alkaline (pH 10) water. Cations were displaced from the sediment by treatment with HCl. A total analysis of cations in the leachate yielded, on the basis of millimoles per 100 g of dry sediment, 150 mmol of Na^+, 5 mmol of K^+, 20 mmol of Mg^{2+}, and 75 mmol of Ca^{2+}. What is the cation exchange capacity of the sediment in milliequivalents per 100 g of dry sediment? Why does H^+ not have to be considered in this case?

   Answer: To get the total cation exchange capacity, multiply the number of millimoles of each monovalent cation by 1 and that of each divalent cation by 2 and take the sum. The content of H^+ is negligible because the solution is alkaline.

   CEC = 150 (for Na^+) + 5 (for K^+) + 2 × 20 (for Mg^{2+}) + 2 × 75 (for Ca^{2+}) = 345 meq/100 g

2. What is the value of $[O_2(aq)]$ for water saturated with a mixture of 50% O_2, 50% N_2 by volume at 25°C and a total pressure of 1.00 atm?

   Answer: The total pressure of the mixture of O_2 and N_2 and corrected for the vapor pressure of water at 25°C is 0.1000 atm – 0.0313 atm = 0.969 atm and partial pressures of each of the two gases are half that or 0.484 atm. The applicable Henry's law constants are 1.28×10^{-3} mol × L^{-1} × atm^{-1} for O_2 and 6.48×10^{-4} mol × L^{-1} × atm^{-1} for N_2. The aqueous concentrations of the gases are given by the following:

   $[O_2(aq)] = 0.484 \text{ atm} \times 1.28 \times 10^{-3} \text{ mol} \times L^{-1} \times \text{atm}^{-1} = 6.20 \times 10^{-4} \text{ mol} \times L^{-1}$

   $[N_2(aq)] = 0.484 \text{ atm} \times 6.48 \times 10^{-4} \text{ mol} \times L^{-1} \times \text{atm}^{-1} = 3.14 \times 10^{-4} \text{ mol} \times L^{-1}$

3. Of the following, the least likely mode of transport of iron(III) in a normal stream is: (a) bound to suspended humic material, (b) bound to clay particles by cation exchange processes, (c) as suspended Fe_2O_3, (d) as soluble Fe^{3+} ion, (e) bound to colloidal clay-humic substance complexes.

   Answer: (d) because of the extremely low solubility of Fe^{3+} ion

4. How does freshly precipitated colloidal iron(III) hydroxide interact with many divalent metal ions in solution?

   Answer: Freshly precipitated iron(III) hydroxide tends to bind with divalent metal cations and remove them from aqueous solution.

5. What stabilizes colloids composed of bacterial cells in water?

   Answer: Hydrogen bonding between water molecules and amino, carboxyl, and –OH groups on the cell surfaces.

6. The solubility of oxygen in water is 14.74 mg/L at 0°C and 7.03 mg/L at 35°C. Estimate the solubility at 50°C.

Answer: Use the Clausius-Clapeyron equation below:

$$\log\frac{C_2}{C_1} = \frac{\Delta H}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Convert the temperatures to K, which for 0°C, 35°C, and 50°C are 273 K, 308 K, and 323 K, respectively and using the concentrations of dissolved O_2 calculate the constant, $\Delta H/2.303R = -773$ K. Using this value in the Clausius-Clapeyron equation, substitute $C_1 = 14.74$ mg/L at $T_1 = 273$ K, set $T_2 = 323$ K, and calculate = 5.37 mg/L at 50°C.

7. What is thought to be the mechanism by which bacterial cells aggregate?

   Answer: A bridging flocculation process involving bridging groups.

8. What is a good method for the production of freshly precipitated MnO_2?

   Answer: Reduction of MnO_4^- ion.

9. A sediment sample was equilibrated with a solution of NH_4^+ ion, and the NH_4^+ was later displaced by Na^+ for analysis. A total of 33.8 milliequivalents of NH_4^+ were bound to the sediment and later displaced by Na^+. After drying, the sediment weighed 87.2 g. What was its CEC in milliequivalents/100 g?

   Answer: (33.8meq/87.2 g)×100 = 38.8 meq/100 g

10. A sediment sample with a CEC of 67.4 milliequivalents/100 g was found to contain the following exchangeable cations in milliequivalents/100 g: Ca^{2+}, 21.3; Mg^{2+}, 5.2; Na^+, 4.4; K^+, 0.7. The quantity of hydrogen ion, H^+, was not measured directly. What was the ECS of H^+ in milliequivalents/100 g?

    Answer:

    ECS of H^+ = CEC - (ECS of Ca^{2+} + ECS of Mg^{2+} + ECS of Na^+ + ECS of K^+)

    ECS of $H^+ = 67.4 - (2 \times 21.3 + 2 \times 5.2 + 4.4 + 0.7) = 9.3$ meq/100 g

11. What is the meaning of *zero point of charge* as applied to colloids? Is the surface of a colloidal particle totally without charged groups at the ZPC?

    Answer: The ZPC is the pH at which the sum of negative charges equals the sum of positive charges so that, although there are still charged groups on the colloidal particle surface, the net charge is zero.

12. The concentration of methane in an interstitial water sample was found to be 150 mL/L at STP. Assuming that the methane was produced by the fermentation of organic matter, $\{CH_2O\}$, what mass of organic matter was required to produce the methane in a liter of the interstitial water?

    Answer: The reaction for the fermentation of organic matter is:

    $2\{CH_2O\} \rightarrow CH_4 + CO_2$

    150 mL CH_4 = 0.150 L $CH_4 = 6.70 \times 10^{-3}$ mol CH_4 produced when = $2\times 6.70 \times 10^{-3} = 1.34 \times 10^{-2}$ mol CH_2O that ferment = 1.34×10^{-2} mol $CH_2O \times 30$ g/mol of CH_2O = 0.402 g CH_2O

13. What is the difference between CEC and ECS?

    Answer: Cation exchange capacity (CEC) expresses the total number of milliequivalents of cations that can be sorbed per 100 g of dry solid whereas exchangeable cation status (ECS) refers to the number of meq of specific cations sorbed per 100 g dry solid.

14. Match the sedimentary mineral from the top list designated with letters with its

conditions of formation from the bottom list designated with numbers:

(A) FeS(*s*) (B) $Ca_5OH(PO_4)_3$ (C) $Fe(OH)_3$ (D) $CaCO_3$

(1) May be formed when anoxic water is exposed to O_2. (2) May be formed when oxic water becomes anoxic. (3) Photosynthesis byproduct. (4) May be formed when wastewater containing a particular kind of contaminant flows into a body of very hard water.

Answer: (A)-2, (B)-4, (C)-1, (D)-3

15. In terms of their potential for reactions with species in solution, how might metal atoms, M, on the surface of a metal oxide, MO, be described?

Answer: The metal atoms can bind with water to produce $M\text{-}OH_2$ and these groups can lose H^+ to produce negatively charged surface $M\text{-}OH^-$ or gain H^+ to produce positively charged $M\text{-}OH_3^+$ surface groups.

16. Air is 20.95% oxygen by volume. If air at 1.0000 atm pressure is bubbled through water at 25°C, what is the partial pressure of O_2 in the water?

Answer: The vapor pressure of water at 25°C is 0.0313 atm, so the air pressure corrected for the vapor pressure of water is 1.0000 atm - 0.0313 atm = 0.9687 atm. The partial pressure of $O_2 = 0.2095 \times 0.9687$ atm = 0.203 atm

17. The volume percentage of CO_2 in a mixture of that gas with N_2 was determined by bubbling the mixture at 1.00 atm and 25°C through a solution of 0.0100 M $NaHCO_3$ and measuring the pH. If the equilibrium pH was 6.50, what was the volume percentage of CO_2?

Answer: The first step is to calculate $[CO_2(aq)]$ from $[H^+]$ and the expression for K_{a1} of CO_2, where $[HCO_3^-] = 0.010$ and $= [H^+]\ 3.16 \times 10^{-7}$. From the calculated value of $[CO_2(aq)]$ use the Henry's law expression to calculate the partial pressure of CO_2, and after correcting for the vapor pressure of water at 25°C (0.0313 atm), calculate the volume percentage of CO_2 in the air.

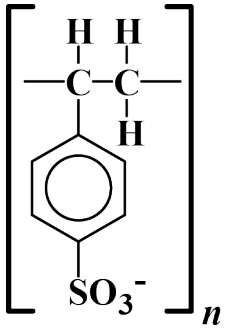
$$[CO_2(aq)] = \frac{[H^+][HCO_3^-]}{K_{a1}} = \frac{3.16 \times 10^{-7} \times 0.010}{4.45 \times 10^{-7}} = 7.10 \times 10^{-3}$$

$$[CO_2(aq)] = K \times P_{CO_2}$$

$$P_{CO_2} = \frac{7.10 \times 10^{-3}\ \text{mol} \times \text{L}^{-1}}{3.38 \times 10^{-2}\ \text{mol} \times \text{L}^{-1} \times \text{atm}^{-1}} = 0.210\ \text{atm}$$

$$\text{Percent } CO_2 = \frac{21.0\%}{0.9687} = 21.7\%$$

18. For what purpose is a polymer with the following general formula used?



Answer: It is used to flocculate colloids

19. Of the following statements, the one that is true regarding colloids is: (A) Hydrophilic colloids consist of aggregates of relatively small molecules, (B) hydrophobic colloids do not have electrical charges, (C) hydrophilic colloids are those formed by clusters of species, such as $H_3C(CH_2)_{16}CO_2^-$, (D) association colloids form micelles, (E) the electrical charges of hydrophobic colloids are insignificant.

    Answer: (D)

20. For a slightly soluble divalent metal sulfate, MSO_4, $K_{sp} = 9.00 \times 10^{-14}$. An excess of pure solid MSO_4 was equilibrated with pure water to give a solution which contains 6.45×10^{-7} mol per liter of dissolved M. Considering these observations the true statement is: (A) MSO_4 has a significant degree of intrinsic solubility, (B) the solubility product, alone, accurately predicts solubility, (C) the value of the solubility product is in error, (D) the concentration of "M" in water must have been in error, (E) the only explanation for the observations is formation of HSO_4^-.

    Answer: If the concentration of the salt in solution were due only to the solubility product, it would be 3.00×10^{-7} mol $\times$ L^{-1}. Since the actual solubility is higher than that, there must be a certain degree of intrinsic solubility, (A).

21. Of the following, the **incorrect** statement regarding sediments and their formation is: (A) Physical, chemical, and biological processes may all result in the deposition of sediments in the bottom regions of bodies of water, (B) indirectly, photosynthesis can result in formation of $CaCO_3$ sediment, (C) oxidation of Fe^{2+} ion can result in formation of an insoluble species that can be incorporated into sediment, (D) sediments typically consist of mixtures of clay, silt, sand, organic matter, and various minerals, and may vary in composition from pure mineral matter to predominantly organic matter, (E) FeS that gets into sediment tends to form at the surface of water in contact with O_2.

    Answer: The incorrect statement is (E)

22. Given that at 25°C, the Henry's law constant for oxygen is 1.28×10^{-3} mol $\times$ L^{-1} $\times$ atm^{-1} and the partial pressure of water vapor is 0.0313 atm, what is the value of $[O_2(aq)]$ for water saturated with a mixture of 33.3% O_2, 66.7% N_2 by volume at 25°C and a total pressure of 1.00 atm in units of mol $\times$ L^{-1}?

    Answer: The total pressure of the mixture of O_2 and N_2 and corrected for the vapor pressure of water at 25°C is 0.1000 atm – 0.0313 atm = 0.969 atm and partial pressure of O_2 is 0.333 $\times$ that or 0.323 atm. The concentration of dissolved O_2 in solution is

    $[O_2(aq)] = 0.323 \text{ atm} \times 1.28 \times 10^{-3} \text{ mol} \times L^{-1} \times atm^{-1} = 6.20 \times 10^{-4} \text{ mol} \times L^{-1}$

23. Match the following regarding colloids from the top list designated with letters with its corresponding match from the bottom list designated with numbers:

    (A) Hydrophilic colloids (B) Association colloids (C) Hydrophobic colloids (D) Noncolloidal

    (1) $CH_3CO_2^-Na^+$ (2) Macromolecular proteins (3) Often removed by addition of salt (4) $CH_3(CH_2)_{16}CO_2^-Na^+$

    Answer: A-2, B-4, C-3, D-1.

Chapter 5
Aquatic Microbial Biochemistry

1. As $CH_3CH_2CH_2CH_2CO_2H$ biodegrades in several steps to carbon dioxide and water, various chemical species are observed. What stable chemical species would be observed as a result of the first step of this degradation process?

   Answer: Straight-chain carboxylic acids such as this one are oxidized two carbon atoms at a time, a process called beta oxidation. The product of the first step is $CH_3CH_2CO_2H$.

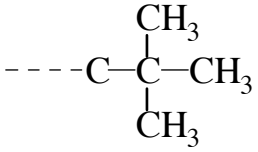
2. Which of the following statements is true regarding the production of methane in water: (A) it occurs in the presence of oxygen, (B) it consumes oxygen, (C) it removes biological oxygen demand from the water, (D) it is accomplished by oxic bacteria, (E) it produces more energy per electron-mole than does oxic respiration.

   Answer: (C)

3. At the time zero, the cell count of a bacterial species mediating oxic respiration of wastes was 1×10^6 cells per liter. At 30 minutes it was 2×10^6; at 60 minutes it was 4×10^6; at 90 minutes, 7×10^6; at 120 minutes, 10×10^6; and at 150 minutes, 13×10^6. From these data, which of the following logical conclusions would you draw? (A) The culture was entering the log phase at the end of the 150-minute period, (B) the culture was in the log phase throughout the 150-minute period, (C) the culture was leaving the log phase at the end of the 150-minute period, (D) the culture was in the lag phase throughout the 150-minute period, (E) the culture was in the death phase throughout the 150-minute period.

   Answer: (C)

4. What may be said about the biodegradability of a hydrocarbon containing the following structure?



   Answer: This quaternary structure is highly resistant to biodegradation.

5. Suppose that the anoxic fermentation of organic matter, $\{CH_2O\}$, in water yields 15.0 L of CH_4 (at standard temperature and pressure). How many grams of oxygen would be consumed by the oxic respiration of the same quantity of $\{CH_2O\}$? (Recall the significance of 22.4 L in chemical reaction of gases.)

   Answer: The reaction for the anoxic fermentation of $\{CH_2O\}$ is $2\{CH_2O\} \rightarrow CH_4 + CO_2$ and the reaction for the oxic respiration of biomass is $\{CH_2O\} + O_2 \rightarrow CO_2 + H_2O$. The calculations involved are the following:

$$\text{mass } \{CH_2O\} = 15.0 \text{ L } CH_4 \times \frac{1 \text{ mol } CH_4}{22.4 \text{ L } CH_4} \times \frac{2 \text{ mol } \{CH_2O\}}{1 \text{ mol } CH_4} \times \frac{30.0 \text{ g } \{CH_2O\}}{1 \text{ mol } \{CH_2O\}} = 40.2 \text{ g } \{CH_2O\}$$

$$\text{mass } O_2 \text{ to degrade } 40.2 \text{ g } \{CH_2O\} = 40.2 \text{ g } \{CH_2O\} \times \frac{1 \text{ mol } \{CH_2O\}}{30.0 \text{ g } \{CH_2O\}} \times \frac{1 \text{ mol } O_2}{1 \text{ mol } \{CH_2O\}} \times \frac{32.0 \text{ g } O_2}{1 \text{ mol } O_2} = 42.9 \text{ g } O_2$$

6. What mass of $FeCO_3(s)$, using Reaction (A) + (4) in Table 5.1, gives the same free energy

yield as 1.00 g of organic matter, using Reaction (A) + (1), when oxidized by oxygen at pH 7.00?

Answer: The reactions to consider here as written for 1 electron mole are:

$FeCO_3 + {}^1/_4O_2 + {}^3/_2H_2O \rightarrow FeOOH + HCO_3^- (10^{-3}) + H^+ \quad \Delta G^0 = -21.0$ kcal

${}^1/_4\{CH_2O\} + {}^1/_4O_2 \rightarrow {}^1/_4CO_2 + {}^1/_4H_2O \; \Delta G^0 = -29.9$ kcal

As seen from the second equation $^1/_4$ mole of $\{CH_2O\}$ = 7.5 grams of $\{CH_2O\}$ yields -29.9 kcal. Thus 1 gram of $\{CH_2O\}$ will yield 3.99 kcal. While according to the first equation 1 mole of $FeCO_3$ (= 115.8 g) yields 21.0 kcal. The mass of $FeCO_3$ needed to yield 3.99 kcal can be calculated to be = 22.0 g. Thus 22.0 g of $FeCO_3$ needs to be oxidized to produce the same amount of free energy as 1.0 g of $\{CH_2O\}$.

7. How many bacteria would be produced after 10 hours by one bacterial cell, assuming exponential growth with a generation time of 20 minutes?

   Answer: In 10 hours there are 600 minutes and with a generation time of 20 minutes, there would be 30 generations, so the number of cells = $2^{30} = 1.07 \times 10^9$.

8. Referring to Reaction 5.11.2, calculate the concentration of ammonium ion in equilibrium with oxygen in the atmosphere and 1.00×10^{-5} M NO_3^- at pH 7.00.

   Answer: The equilibrium reaction is

   ${}^1/_4O_2(g) + {}^1/_8NH_4^+ \rightarrow {}^1/_8NO_3^- + {}^1/_4H^+ + {}^1/_8H_2O$

   for which the equilibrium constant is$10^{7.59}$. Correcting for the vapor pressure of water, the pressure of O_2 in air at 1.00 atm atmospheric pressure at 25°C is 0.203 atm and the solution to the problem is the following:

$$\frac{[H^+]^{1/4}[NO_3^-]^{1/8}}{P_{O_2}^{1/4}[NH_4^+]^{1/8}} = 10^{7.59} = 3.89\times10^7 \qquad [NH_4^+]^{1/8} = \frac{(1\times10^{-7})^{1/4}\times(1\times10^{-5})^{1/8}}{0.203^{1/4}\times3.89\times10^7}$$

$$[NH_4^+]^{1/8} = 1.615 \times 10^{-10} \qquad [NH_4^+] = 4.63 \times 10^{-79}$$

   In any real system, the value of $[NH_4^+]$ would never get this low, but at any condition approaching equilibrium between NH_4^+ and NO_3^- in contact with atmospheric oxygen the concentration of $[NH_4^+]$ would be extremely low.

9. When a bacterial nutrient medium is inoculated with bacteria grown in a markedly different medium, the lag phase (Fig. 5.4) often is quite long, even if the bacteria eventually grow well in the new medium. Can you explain this behavior?

   Answer: The bacteria may have to evolve to a form that can grow well in the medium in which they are placed.

10. Most plants assimilate nitrogen as nitrate ion. However, ammonia (NH_3) is a popular and economical fertilizer. What essential role do bacteria play when ammonia is used as a fertilizer? Do you think any problems might occur when using ammonia in a waterlogged soil lacking oxygen?

    Answer: Bacteria mediate the oxidation of ammonia to nitrate ion, which can be assimilated by plants. In a waterlogged soil insufficient oxygen may be available to enable nitrifying bacteria to oxidize ammonium nitrogen to nitrate.

11. Why is the growth rate of bacteria as a function of temperature (Fig. 5.7) not a symmetrical curve?

Answer: From lower temperatures, the growth rate of bacteria increases with increasing temperature, then drops abruptly when temperatures reach values in which bacterial enzymes are destroyed.

12. Discuss the analogies between bacteria and a finely divided chemical catalyst.

    Answer: A finely divided catalyst presents a large surface area upon which chemical species may react. Similarly, small bacterial cells have large surface/volume ratios.

13. Would you expect autotrophic bacteria to be more complex physiologically and biochemically than heterotrophic bacteria? Why?

    Answer: A reason to expect autotrophic bacteria to be more complex is that they have to convert very simple inorganic materials to complex biomolecules.

14. Wastewater containing 8 mg/L O_2 (atomic mass O = 16), 1.00×10^{-3} M NO_3^-, and 1.00×10^{-2} M soluble organic matter, $\{CH_2O\}$, is stored isolated from the atmosphere in a container richly seeded with a variety of bacteria. Assume that denitrification is one of the processes which will occur during storage. After the bacteria have had a chance to do their work, which of the following statements will be true? (A) No $\{CH_2O\}$ will remain, (B) some O_2 will remain, (C) some NO_3^- will remain, (D) denitrification will have consumed more of the organic matter than oxic respiration, (E) the composition of the water will remain unchanged.

    Answer: (D) because nitrate is the more abundant oxidant

15. Of the four classes of microorganisms—algae, fungi, bacteria, and virus—which has the least influence on water chemistry?

    Answer: Virus would have the least influence because they are very small entities that function only in living cells of organisms

16. Figure 5.3 shows the main structural features of a bacterial cell. Which of these do you think might cause the most trouble in water-treatment processes such as filtration or ion exchange, where the maintenance of a clean, unfouled surface is critical? Explain.

    Answer: The capsule or slime layer protects the bacteria and helps the bacterial cells to adhere to surfaces. The material in this layer can clog filters and coat surfaces causing trouble in water treatment systems.

17. A bacterium capable of degrading 2,4-D herbicide was found to have its maximum growth rate at 32°C. Its growth rate at 12°C was only 10% of the maximum. Do you think there is another temperature at which the growth rate would also be 10% of the maximum? If you believe this to be the case, of the following temperatures, choose the one at which it is most plausible for the bacterium to also have a growth rate of 10% of the maximum: 52°C, 37°C, 8°C, 20°C.

    Answer: In reference to the asymmetrical plot of growth rate as a function of temperature in Figure 5.7, there would be another point at a temperature somewhat higher than the optimum temperature where the growth rate is 10% of the maximum. The temperature of 52°C is too hot and the bacteria would probably be killed at such a temperature so the most likely answer is 37°C.

18. The day after a heavy rain washed a great deal of cattle feedlot waste into a farm pond, the following counts of bacteria were obtained in which thousands of viable cells per mL of water are given in parentheses after each time listed:

    6:00 a.m. (0.10), 7:00 a.m. (0.11), 8:00 a.m. (0.13), 9:00 a.m. (0.16), 10:00 a.m. (0.20), 11:00

a.m. (0.40), 12:00 Noon (0.80), 1:00 p.m. (1.60), 2:00 p.m. (3.20)

To which portion of the bacterial growth curve, Figure 5.3, does this time span correspond?

Answer: For the first four hours, the bacteria are in a lag phase and beyond that in the log phase.

19. Addition of which two half-reactions in Table 5.1 is responsible for: (A) elimination of an algal nutrient in secondary sewage effluent using methanol as a carbon source, (B) a process responsible for a bad-smelling pollutant when bacteria grow in the absence of oxygen, (C) A process that converts a common form of commercial fertilizer to a form that most crop plants can absorb, (D) a process responsible for the elimination of organic matter from wastewater in the aeration tank of an activated sludge sewage-treatment plant, (E) a characteristic process that occurs in the anoxic digester of a sewage treatment plant.

    Answer: (A) 1 + C, (B) 1 + E, (C) 3 + A, (D) 1 + A, (E) 1 + F

20. What is the surface area in square meters of 1.00 gram of spherical bacterial cells, 1.00 μm in diameter, having density of 1.00 g/cm^3?

    Answer: The volume occupied by 1.00 g of bacterial cells = 1.00 cm^3 = 1.00 × 10^{-6} m^3. Volume of one bacterial cell = $4/3\pi r^3$ = 5.23 × 10^{-19} m^3, the number of bacterial cells in 1.00 × 10^{-6} m^3 = 1.91 × 10^{12}. The surface area of one spherical bacterial cell = $4\pi r^2$ = 3.14 × 10^{-12} m^2 and the surface area of all the bacterial cells in 1.00 cm^3 of bacteria = 1.91 × 10^{12} × 3.14 × 10^{-12} = 5.99 m^2.

21. What is the purpose of exoenzymes in bacteria?

    Answer: Exoenzymes act to metabolize substances outside the bacterial cell

22. Match each species of bacteria listed by letters in the top row with its function from the numbered list below:

    (A) *Spirillum lipoferum* (B) *Rhizobium* (C) *Thiobacillus ferrooxidans* (D) *Desulfovibrio*

    (1) Reduces sulfate to H_2S (2) Catalyzes oxidation of Fe^{2+} to Fe^{3+} (3) Fixes nitrogen in grasses (4) On legume roots

    Answer: (A)-3, (B)-4, (C)-2, (D)-1

23. What factors favor the production of methane in anoxic surroundings?

    Answer: Availability of degradable organic matter and absence of oxidants including molecular oxygen, sulfate, and nitrate

24. Below are listed three kinds of microorganisms, and below that are listed with numbers several chemical species or energy sources. In parentheses to the <u>left</u> of each kind of microorganism, place the numbers corresponding to at least <u>two</u> things that the micoorganism might <u>need</u> or <u>use</u>. In parentheses to the <u>right</u> of each kind of microorganism, place the numbers corresponding to at least <u>two</u> things that the microorganism might produce.

    ( ) Algae ( )
    ( ) Aerobic (oxic), nonphotosynthetic, autotrophic *Gallionella* bacteria ( )
    ( ) Anoxic, heterotrophic bacteria ( )

    1. CO_2, 2. $h\nu$, 3. O_2, 4. $\{CH_2O\}$, 5. CH_4, 6. $Fe(OH)_3$, 7. electron acceptor other than O_2.

    Answer:

    (1,2) Algae (3,4)

(3,Fe(II)) Aerobic (oxic), nonphotosynthetic, autotrophic *Gallionella* bacteria (1,6)
(4,7) Anaerobic (anoxic), heterotrophic bacteria (1,5)

25. Bacteria growing in the log phase on a waste in water were assayed at a particular time, t_0, and found to number 3.01×10^5 cells/mL. At 90 minutes after t_0 the count was 2.41×10^6 cells/mL. The best estimate of the following of the bacterial population at 60 minutes after t_0 is: (A) 4.20×10^5, (B) 8.25×10^5, (C) 6.48×10^5, (D) 1.20×10^6, (E) 3.21×10^6

Answer: (D)

26. Consider a type of bacteria that derive energy by mediating the oxidation of sulfides, such as H_2S, FeS, or FeS_2, with molecular oxygen, O_2. Such bacteria (A) are most likely heterotrophic, (B) cannot be autotrophic, (C) should be thermophilic, (D) should be acid-tolerant, (E) cannot exist.

Answer: (D)

27. The growth rate of bacteria, "G," given in parentheses was plotted *vs.* an unidentified parameter, "X," giving the following values in which both G and X are in arbitrary units:

X=5 (100),X=10 (200), X=15 (300), X=20 (400), X=25 (500), X=30 (600), X=35(700), X=40(700), X=45 (350), X=50 (25)

Based on the above data X is most likely (A) time, showing the bacteria with a generation time of 5 units of X, (B) nutrient concentration, (C) waste product, (D) pH, (E) temperature.

Answer: (E)

28. Of the following, the **untrue** statement pertaining to biodegradation of organic matter is (A) epoxidation consists of adding an oxygen atom between two C atoms, (B) oxidation of hydrocarbon chains tends to occur 2 carbon atoms at a time, (C) esterases are a specific category of hydrolase ions, (D) carbon atoms bonded to 3 or 4 other carbon atoms are especially susceptible to microbial epoxidation, (E) exoenzymes are involved in the biodegradation of cellulose.

Answer: (D)

29. Of the following, the **untrue** statement is (A) all fungi and protozoans are chemoheterotrophs, (B) photoheterotrophs that use photoenergy, but are dependent on organic matter as a carbon source are especially abundant and widespread, (C) chemoautotrophs use CO_2 for biomass and oxidize substances such as NH_4^+ for energy, (D) algae are photoautotrophs, (E) some bacteria, such as cyanobacteria, perform photosynthesis.

Answer: (B)

30. The reaction, $4FeS(s) + 9O_2 + 10H_2O \rightarrow 4Fe(OH)_3\ (s) + 4SO_4^{2-} + 8H^+$ (A) illustrates sulfate reduction, (B) is a means for autotrophic *Gallionella* bacteria to obtain energy, (C) illustrates the action of heterotrophic bacteria, (D) is not mediated by bacteria, (E) is written for 1 electron-mole.

Answer: (B)

Chapter 6
Water Pollutants and Water Pollution

1. Which of the following statements is true regarding chromium in water: (A) chromium(III) is suspected of being carcinogenic, (B) chromium(III) is less likely to be found in a soluble form than chromium(VI), (C) the toxicity of chromium(III) in electroplating wastewaters is decreased by oxidation to chromium(VI), (D) chromium is not an essential trace element, (E) chromium is known to form methylated species analogous to methylmercury compounds.

   Answer: (B)

2. What do mercury and arsenic have in common in regard to their interactions with bacteria in sediments?

   Answer: They are both converted to methylated forms by anoxic bacteria

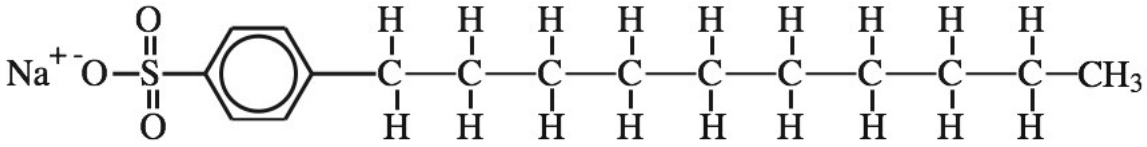
3. What are some characteristics of radionuclides that make them especially hazardous to humans?

   Answer: They produce ionizing radiation and may be in elemental forms found in the body (radioactive iodine that accumulates in the thyroid) or elements that substitute for those in the body (radioactive strontium that substitutes for bone calcium).

4. To what class do pesticides containing the following group belong?

   Answer: Carbamates

5. Consider the following compound:



   Which of the following characteristics is not possessed by the compound: (A) one end of the molecule is hydrophilic and the other end in hydrophobic, (B) surface-active qualities, (C) the ability to lower surface tension of water, (D) good biodegradability, (E) tendency to cause foaming in sewage treatment plants.

   Answer: (E)

6. A certain pesticide is fatal to fish fingerlings at a level of 0.50 parts per million in water. A leaking metal can containing 5.00 kg of the pesticide was dumped into a stream with a flow of 10.0 liters per second moving at 1 kilometer per hour. The container leaks pesticide at a constant rate of 5 mg/sec. For what distance (in km) downstream is the water contaminated by fatal levels of the pesticide by the time the container is empty?

   Answer: The pesticide concentration in the contaminated water is 0.50 ppm = 0.50 mg/L. At a leakage rate of 5 mg/sec, the time taken to empty the container is $(5.00 \times 10^6$ mg)/5 mg/sec = 1.00×10^6 sec = 278 hr during which time all the water flowing at 10.0 L/sec

over the container will become contaminated with 0.5 ppm of the pesticide. The distance downstream contaminated by the pesticide is 278 hr × 1 km/hr = 278 km.

7. Give a reason that Na_3PO_4 would not function well as a detergent builder, whereas $Na_3P_3O_{10}$ is satisfactory, though it is a source of pollutant phosphate.

   Answer: Although both bind with calcium (water hardness), the anion of $Na_3P_3O_{10}$ forms a soluble chelate with Ca^{2+} ion whereas Na_3PO_4 forms a potentially troublesome precipitate of calcium phosphate.

8. Of the compounds $CH_3(CH_2)_{10}CO_2H$, $(CH_3)_3C(CH_3)_2CO_2H$, $CH_3(CH_2)_{10}CH_3$, and ϕ-$(CH_2)_{10}CH_3$ (where ϕ represents a benzene ring), which is the most readily biodegradable?

   Answer: $CH_3(CH_2)_{10}CO_2H$ would be the most readily biodegradable because of its straight chain and carboxylic acid group, which is readily metabolized by bacteria forming progressively shorter chain acids and finally CO_2.

9. A pesticide sprayer got stuck while trying to ford a stream flowing at a rate of 136 liters per second. Pesticide leaked into the stream for exactly 1 hour and at a rate that contaminated the stream at a uniform 0.25 ppm of methoxychlor. How much pesticide was lost from the sprayer during this time?

   Answer: Each second 136 L of water was contaminated by 0.25 mg/L pesticide so:

   Mass pesticide = 136 L/sec × 3600 sec × 0.25 mg/L = 122,400 mg = 122 g

10. A sample of water contaminated by the accidental discharge of a radionuclide used for medicinal purposes showed an activity of 12,436 counts per second at the time of sampling and 8,966 cps exactly 30 days later. What is the half-life of the radionuclide?

    Answer: Use the two formulas $A = A_0e^{-\lambda t}$ and

    $$t_{1/2} = \frac{0.693}{\lambda}$$

    where A_0 = 12,436 cps, A = 8966 cps and t = 30 days to calculate $\lambda = 0.0109\ day^{-1}$ and $t_{1/2}$ = 63.5 day λ

    $\ln A = \ln A_0\ \lambda t \quad \ln 8966 = \ln 12436 - 30\ \lambda$

11. What are the two reasons that soap is environmentally less harmful than ABS surfactant used in detergents?

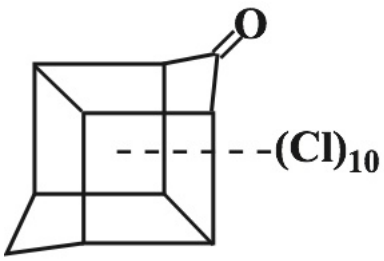
    Answer: Soap precipitates from solution with Ca^{2+} ion and is much more biodegradable than ABS surfactant

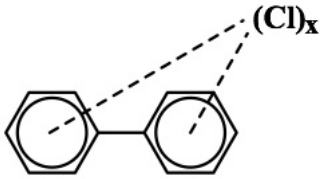
12. What is the exact chemical formula of the specific compound designated as PCB?

    Answer: PCBs have variable formulas with a number of congeners produced by substitution of Cl for H on biphenyl.

13. Match each compound designated by a letter in the top list with the description corresponding to its description or characteristic designated by a number below.

    (A) CdS (B) $(CH_3)_2AsH$

(C) 

(D) 

(1) Pollutant released to a U.S. stream by a poorly controlled manufacturing process.

(2) Insoluble form of a toxic trace element likely to be found in anaerobic sediments.

(3) Common environmental pollutant formerly used as a transformer coolant.

(4) Chemical species thought to be produced by bacterial action.

Answer: (A)-2, (B)-4, (C)-1, (D)-3

14. A radioisotope has a nuclear half-life of 24 hours and a biological half-life of 16 hours (half of the element is eliminated from the body in 16 hours). A person accidentally swallowed sufficient quantities of this isotope to give an initial "whole body" count rate of 1000 counts per minute. What was the count rate after 16 hours?

    Answer: If the isotope had an "infinitely long" nuclear half-life, after exactly 1 biological half-life (16 hr) the whole body count rate would be 1000 cpm/2 = 500 cpm a value that can be taken as A_0 to calculate A after 16 hours in the relationship $A = A_0e^{-\lambda t}$. Using the nuclear half-life of 24 hours, calculate $\lambda = 0.693/t_{1/2}$ which gives A = 315 cpm.

15. What is the primary detrimental effect upon organisms of salinity in water arising from dissolved NaCl and Na_2SO_4?

    Answer: Increased salinity causing harm due to osmotic effects

16. Give a specific example of each of the following general classes of water pollutants: (A) trace elements, (B) metal-organic combinations, (C) pesticides

    Answer: (A) Arsenic in drinking water; (B) dimethylmercury, $Hg(CH_3)_2$; (C) atrazine agricultural herbicide in groundwater

17. A polluted water sample is suspected of being contaminated with one of the following: soap, ABS surfactant, or LAS surfactant. The sample has a very low BOD relative to its TOC. Which is the contaminant?

    Answer: Both soap and LAS surfactants have relatively high BODs whereas ABS surfactant does not biodegrade well and is probably the contaminant.

18. Of the following, the one that is **not** a cause of, or associated with eutrophication is (A) eventual depletion of oxygen in the water, (B) excessive phosphate, (C) excessive algal growth, (D) excessive nutrients, (E) excessive O_2.

    Answer: (E)

19. Match the pollutants from the top list with effects or other significant aspects on the bottom list, below:

    (A) Salinity (B) Alkalinity (C) Acidity (D) Nitrate

    (1) Excessive productivity (2) Can enter water from pyrite or from the atmosphere (3) Osmotic effects on organisms (4) From soil and mineral strata

    Answer: (A)-3, (B)-4, (C)-2, (D)-1

20. Of the following heavy metals, choose the one most likely to have microorganisms involved in its mobilization in water and explain why this is so: (A) Lead, (B) mercury, (C) cadmium, (D) chromium, (E) zinc.

    Answer: (B) Mercury because of the formation of soluble methylated forms by anoxic bacteria

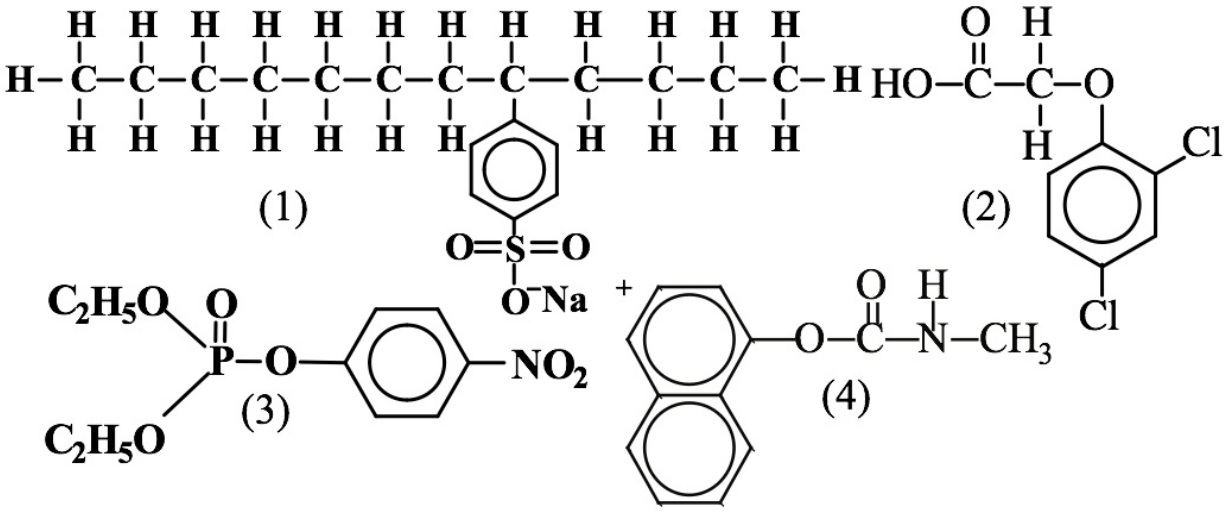
21. Of the following, the true statement is (A) eutrophication results from the direct discharge of toxic pollutants into water, (B) treatment of a lake with phosphates is a process used to deter eutrophication, (C) alkalinity is the most frequent limiting nutrient in eutrophication, (D) eutrophication results from excessive plant or algal growth, (E) eutrophication is generally a beneficial phenomenon because it produces oxygen.

    Answer: (D)

22. Of the following, the statement that is **untrue** regarding radionuclides in the aquatic environment is (A) they emit ionizing radiation, (B) they invariably come from human activities, (C) radionuclides of "life elements," such as iodine-131, are particularly dangerous, (D) normally the radionuclide of most concern in drinking water is radium, (E) they may originate from the fission of uranium nuclei.

    Answer: (B)

23. From the formulas below match the following: (A) Lowers surface tension of water, (B) a carbamate, (C) a herbicide, (D) a non-carbamate insecticide.



    Answer: (A)-(1), (B)-(4), (C)-(2), (D)-(3)

24. Polychlorinated biphenyls, PCBs, (A) consist of over 200 congeners with different numbers of chlorine atoms, (B) are noted for their biological instability and, therefore, toxicity, (C) occur primarily as localized pollutants, (D) are not known to undergo any biodegradation processes, (E) had no common uses, but were produced as manufacturing byproducts.

    Answer: (A)

Chapter 7
World Water Crisis and Climate Change: Water Renovation and Recycling

1. Consider the equilibrium reactions and expressions covered in Chapter 2. How many moles of NTA should be added to 1000 liters of water having a pH of 9 and containing CO_3^{2-} at 1.00×10^{-4} M to prevent precipitation of $CaCO_3$? Assume a total calcium level of 40 mg/L.

   Answer: At 40 mg/L, the concentration of calcium in solution is 4.00×10^{-2} g/L/40.0 g/mol = 1.00×10^{-3} mol/L. Enough NTA must be added to bind with all the Ca^{2+} so that the total NTA added is 1.00×10^{-3} mol/L or 1.00 mol in 1000 L.

2. What is the purpose of the return sludge step in the activated sludge process?

   Answer: The return sludge maintains a high level of the microorganisms required to biodegrade the sludge in the aeration tank.

3. What are the two processes by which the activated sludge process removes soluble carbonaceous material from sewage?

   Answer: Some of the soluble organic matter is incorporated into biomass that settles from suspension and some of the carbon in the soluble organic matter is converted to carbon dioxide.

4. Why might hard water be desirable as a medium if phosphorus is to be removed by an activated sludge plant operated under conditions of high aeration?

   Answer: Hard water would provide the Ca^{2+} required to precipitate the phosphate as hydroxyapatite, $CaOH(PO_4)_3$

5. How does reverse osmosis differ from a simple sieve separation or ultrafiltration process?

   Answer: Reverse osmosis depends upon the affinity of the membrane for water and its rejection of ions.

6. How many liters of methanol would be required daily to remove the nitrogen from a 200,000-L/day sewage treatment plant producing an effluent containing 50 mg/L of nitrogen? Assume that the nitrogen has been converted to NO_3^- in the plant. The denitrifying reaction is Reaction 7.12.7.

   $6NO_3^- + 5CH_3OH + 6H^+ \rightarrow 3N_2(g) + 5CO_2 + 13H_2O$

   At 50 mg/L N the number of moles of N in 200,000 L of wastewater is 0.050 g/L × 2.00×10^5 L/14.0 g/mol = 714 mol N. From the mole ratios shown in the reaction, $^5/_6 \times 714$ = 595 mol of CH_3OH, molar mass 32 g/mol would be required giving the following:

   Mass of CH_3OH = 595 mol × 32 g/mol = 1.90×10^4 g = 19.0 kg CH_3OH per day

   The density of CH_3OH is 0.791 kg/L so that the volume of CH_3OH required is

   Volume = 19.0 kg/0.791 kg/L = 24.0 L daily

7. Discuss some of the advantages of physical-chemical treatment of sewage as opposed to biological wastewater treatment. What are some disadvantages?

   Answer: Lower capital costs, less land requirements, better handling of toxic materials

and overloads are some of the advantages, while requirement of careful operator control and consumption of higher amounts of energy and chemicals are the disadvantages.

8. Why is recarbonation necessary when water is softened by the lime-soda process?

   Answer: To prevent precipitation of $CaCO_3$ which can cause scaling of pipes.

9. Assume that a waste contains 300 mg/L of biodegradable $\{CH_2O\}$ and is processed through a 200,000-L/day sewage-treatment plant which converts 40% of the waste to CO_2 and H_2O. Calculate the volume of air (at 25°C, 1 atm) required for this conversion. Assume that the O_2 is transferred to the water with 20% efficiency.

   Answer: In 200,000 L of water containing 0.300 g/L $\{CH_2O\}$, molar mass 30.0 g/mol, and of which 40% of the $\{CH_2O\}$ undergoes oxidation to CO_2 and H_2O, the moles of $\{CH_2O\}$ undergoing oxidation are the following:

   The reaction is $\{CH_2O\} + O_2 \rightarrow CO_2 + H_2O$

   0.400×0.300 g/L $\times$ 200,000 L $\times$ 1 mol/30.0 g = 800 mol $\{CH_2O\}$

   From the stoichiometry of the biodegradation reaction, 800 mol of O_2 would be required. However, air is only 20% O_2 so 800 mol/0.200 = 4000 mol of air. Furthermore, the air is transferred to the water at only 20% efficiency bringing the number of moles of air to 4000/0.200 = 20,000 mol of air. Since the volume of a mole of air at 25°C and 1 atm pressure is 24.4 L, the volume of air would be 2.00×10^4 mol $\times$ 24.4 L/mol = 4.88×10^5 L/day.

10. If all of the $\{CH_2O\}$ in the plant described in Question 9 could be converted to methane by anoxic digestion, how many liters of methane (STP) could be produced daily?

    Answer: The total amount of $\{CH_2O\}$ processed by the plant in one day is

    0.300 g/L $\times$ 200,000 L $\times$ 1 mol/30.0 g = 2000 mol $\{CH_2O\}$

    The reaction for the production of methane is $2\{CH_2O\} \rightarrow CO_2(g) + CH_4(g)$

    If all the $\{CH_2O\}$ underwent this reaction,

    Mol CH_4 = 2000 mol $\{CH_2O\}$ $\times$ 1 mol CH_4/2 mol $\{CH_2O\}$ = 1000 mol CH_4

    Volume CH_4 = 1000 mol CH_4 $\times$ 22.4 L CH_4/mol CH_4 = 22,400 L CH_4

11. Assuming that aeration of water does not result in the precipitation of calcium carbonate, of the following, which ones of the following would not be removed by aeration: hydrogen sulfide, carbon dioxide, volatile odorous bacterial metabolites, alkalinity, iron?

    Answer: Alkalinity

12. In which of the following water supplies would moderately high water hardness be most detrimental: municipal water; irrigation water; boiler feedwater; drinking water (in regard to potential toxicity).

    Answer: Boiler feedwater because of scaling

13. Which solute in water is commonly removed by the addition of sulfite or hydrazine?

    Answer: Dissolved O_2

14. A wastewater containing dissolved Cu^{2+} ion is to be treated to remove copper. Which of the following processes would *not* remove copper in an insoluble form; lime precipitation; cementation; treatment with NTA; ion exchange; reaction with metallic Fe.

    Answer: Treatment with NTA

15. Match each water contaminant in the top lettered list with its preferred method of

removal in the numbered list below.

(A) Mn^{2+} (B) Ca^{2+} and HCO_3^- (C) Trihalomethane compounds (D) Mg^{2+}

(1) Activated carbon (2) Raise pH by addition of Na_2CO_3 (3) Addition of lime (4) Oxidation

Answer: (A)-(4), (B)-(3), (C)-(1), (D)-(2)

16. A cementation reaction employs iron to remove Cd^{2+} present at a level of 350 mg/L from a wastewater stream. Given that the atomic mass of Cd is 112.4 and that of Fe is 55.8, how many kg of Fe are consumed in removing all the Cd from 4.50×10^6 liters of water?

Answer: The calculation is the following:

4.50×10^6 L × 0.350 g Cd/L/112.4 g Cd/mol Cd = 1.40×10^4 mol Cd

From the stoichiometry of the reaction $Cd^{2+} + Fe \rightarrow Cd + Fe^{2+}$

Mass Fe = 1.40×10^4 mol Cd × 1 mol Fe/mol Cd × 0.0558 kg Fe/mol Fe = 78.1 kg Fe

17. Consider municipal drinking water from two different kinds of sources, one a flowing, well-aerated stream with a heavy load of particulate matter, and the other an anoxic groundwater. Describe possible differences in the water treatment strategies for these two sources of water.

Answer: The surface water would need to be filtered, possibly with the addition of coagulants to remove particles, but it has already been aerated by the stream. The anoxic groundwater would be well filtered in the aquifer, but may contain soluble Fe^{2+} and Mn^{2+} along with odorous volatile constitutents that would be removed by aeration.

18. In treating water for industrial use, consideration is often given to "sequential use of the water." What is meant by this term? Give some plausible examples of sequential use of water.

Answer: Sequential use of water refers to taking water that has been minimally contaminated and using it for some purpose that does not require such good quality water before it is discharged. One common example is to use for irrigation treated sewage effluent that has been through a municipal water system. Water used for some processing operations can be employed as cooling water.

19. Active biomass is used in the secondary treatment of municipal wastewater. Describe three ways of supporting a growth of the biomass, contacting it with wastewater, and exposing it to air.

Answer: In the activated sludge process, the active biomass is suspended in the wastewater by air pumped into the water. A trickling filter has biomass coated onto a support that is exposed to the atmosphere and the water is run over the immobilized biomass. In a rotating biological contactor, the biomass is coated onto discs that rotate so that half of each disc is in contact with wastewater and the other half in contact with air at any given time.

20. Using appropriate chemical reactions for illustration, show how calcium present as the dissolved HCO_3^- salt in water is easier to remove than other forms of hardness, such as dissolved $CaCl_2$.

Answer: Calcium present in water as the bicarbonate salt (temporary hardness) can be removed as solid calcium carbonate by two methods that do not work for calcium present as salts such as the chloride. These are the following:

Heating to drive off CO_2: $Ca^{2+} + 2HCO_3^- + \text{heat} \rightarrow CaCO_3(s) + CO_2(g) + H_2O$

Addition of $Ca(OH)_2$ (lime): $Ca^{2+} + 2HCO_3^- + Ca(OH)_2 \rightarrow 2CaCO_3(s) + 2H_2O$

21. Match the pollutant or impurity from the top lettered list on the left with a reagent used to treat or remove it in the numbered list below:

(A) Bacteria (B) PCB (C) H_2S (D) Colloidal matter

(1) Ozone (2) $Al_2(SO_4)_3$ (3) Activated carbon (4) Air

Answer: (A)-(1), (B)-(3), (C)-(4), (D)-(2)

22. Match each water constituent from the top lettered list with the substance that it treats or removes in the numbered list below.

(A) Oxygen (B) Calcium, Ca^{2+} (C) $\{CH_2O\}$ (D) Colloidal solids

(1) Live microorganisms (2.) Phosphate, PO_4^{3-} (3) Hydrazine (H_4N_2) or sulfite (SO_3^{2-})
(4) $Al_2(SO_4)_3 \cdot 18H_2O$

Answer: (A)-(3), (B)-(2), (C)-(1), (D)-(4)

23. Regarding secondary wastewater treatment, the true statement of the following is (A) the activated sludge process is predominantly a physical/chemical process, (B) trickling filters make use of a mass of biological sludge that is continuously pumped over the filter, (C) excess sludge from activated sludge treatment is likely to undergo the process represented by $2\{CH_2O\} \rightarrow CH_4 + CO_2$, (D) the activated sludge process gets rid of all of the sludge as soon as it is made, (E) the trickling filter is an anaerobic (oxygen-free) treatment process.

Answer: (C)

24. Of the following, the true statement pertaining to water disinfection is (A) disinfection with ozone is particularly desirable because the ozone persists throughout the water distribution system, (B) disinfection with ozone is noted for producing toxic organic byproducts, (C) organic substances are left in water to be treated by chlorine to retain disinfecting capacity in the water, (D) the main disadvantage of chlorination of water is that Cl_2 gas is the only effective chlorinating agent, (E) chlorine dioxide, ClO_2, is an effective water disinfectant that does not produce impurity trihalomethanes in water treatment.

Answer: (E)

25. Of the following, designate the technique **least likely** to significantly lower the concentration of heavy metals in water and explain your choice: (A) Cementation, (B) anion exchange, (C) addition of S^{2-}, (D) biological waste treatment, (E) lime.

Answer: (B)

26. Of the following, designate the **least likely** to be effective in reducing total levels of dissolved ions (salts) from water and explain your choice: (A) Reverse osmosis, (B) cation exchange followed by anion exchange, (C) distillation (D) ion exchange as practiced for water softening, (E) electrodialysis.

Answer: (D)

27. Using internet resources, attempt to find instances in which deliberate poisoning of water supplies has been used as a tactic for warfare or terrorism.

Answer: Given the potential of poisoning of water supplies to cause harm, there are remarkably few instances where this has happened in modern times. One instance of historical interest dates from about 590 BC during the First Sacred War in Greece when Athens and the Amphictionic League poisoned the water supply of the besieged town of Kirrha with hellebore plant, which contains toxic helleborin and helleborein glycosides that are toxic to the cardiovascular system.

28. Bottled water is a product with enormous annual sales. What are the advantages of using this source of drinking water? What are the environmental disadvantages of this product?

Answer: A potential advantage can be safety and taste in cases where the municipal water may be contaminated or have taste and odor problems. Delivering water in individual bottles is an inefficient means of getting it and results in substantial solid waste problems with discarded bottles. Bottled water is not necessarily held to the same quality standards as those that apply to municipal systems.

Chapter 8
The Atmosphere and Atmospheric Chemistry

1. What phenomenon is responsible for the temperature maximum at the boundary of the stratosphere and the mesosphere?

   Answer: The absorption of energy from ultraviolet radiation, primarily O_2 and O_3, warms this region.

2. What function does a third body serve in an atmospheric chemical reaction?

   Answer: It absorbs excess energy from an energetic newly formed or excited molecule or radical preventing it from dissociating

3. Why does the lower boundary of the ionosphere lift at night?

   Answer: Without sunlight new ions are not being formed and existing ions (primarily positively charged species and negative electrons) become neutralized. This happens first in the lower regions of the ionosphere where the pressure is relatively higher and there is a greater abundance of ions to be neutralized.

4. Considering the total number of electrons in NO_2, why might it be expected that the reaction of a free radical with NO_2 is a chain-terminating reaction?

   Answer: The NO_2 molecule has an uneven number of electrons meaning that one of its valence electrons is unpaired and available to form a bond with the unpaired electron in a radical to produce a stable species.

5. It may be argued that wind energy, which is now used by growing numbers of large turbines to generate renewable electricity, is actually a form of solar energy. Explain on the basis of meteorological phenomena the rationale for this argument.

   Answer: The sun heats masses of air causing expansion, which is manifested by wind blowing.

6. Suppose that 22.4 liters of air at STP is used to burn 1.50 g of carbon to form CO_2, and that the gaseous product is adjusted to STP. What is the volume and the average molar mass of the resulting mixture?

   Answer: The reaction here is given by: $C + O_2 \rightarrow CO_2$, and since the mol:mol ratio of C to CO_2 is 1:1, the moles of CO_2 formed = moles of C present. The moles of C = 0.125 and the mass of the CO_2 moles formed = 0.125 mol × 44 g/mol = 5.5 g. Prior to the combustion reaction, 1.00 mol of air (22.4 L) contains 0.21 moles of O_2, after the combustion reaction is complete the air will contain 0.21 - 0.125 = 0.085 moles of O_2 (= 0.085 moles × 32 g/mol = 2.72 g), the air will still contain 0.78 moles of N_2 (=21.8 g) and 0.4 g of Ar. Thus the mass of the air after the combustion = 2.72 g + 21.8 g + 0.4 g + 5.5 g = 30.4 g = average molar mass. Since there is still one mole of air left (the oxygen was converted to CO_2 on a 1:1 basis resulting in no net change), the volume of this air will still be 22.4 L.

7. If the pressure is 0.01 atm at an altitude of 38 km and 0.001 at 57 km, what is it at 19 km (ignoring temperature variations)?

   Answer: The equation relating pressure at a given altitude, P_h, is a log function of the

altitude, h. Since P_h decreases by 1 log unit (factor of 10) for an increase in altitude of 19 km from 38 km to 57 km, it would be higher by a factor of 10 at an altitude 19 km lower than 38 km at 19 km. Therefore, at 19 km the pressure would be 0.1 atm.

8. Measured in μm, what are the lower wavelength limits of solar radiation reaching the earth; the wavelength at which maximum solar radiation reaches the earth; and the wavelength at which maximum energy is radiated back into space?

   Answer: The lower wavelength of solar radiation reaching Earth's surface is around 200 nanometers (nm), the maximum intensity of incoming light is around 500 nm, and the maximum intensity of outgoing infrared radiation is around 10 micrometers (μm).

9. Of the species O, HO*•, NO_2*, H_3C•, and N^+, which could most readily revert to a nonreactive, "normal" species in total isolation?

   Answer: NO_2* because it is an excited state of the NO_2 molecule and could revert to the stable ground state by emitting a photon. Each of the other species would have to react with something else to become a stable species which could not happen in total isolation.

10. Of the gases neon, sulfur dioxide, helium, oxygen, and nitrogen, which shows the most variation in its atmospheric concentration?

    Answer: Sulfur dioxide because it is emitted to the atmosphere as a pollutant and undergoes atmospheric reactions, such as formation of H_2SO_4, that remove it from the atmosphere.

11. A 12.0-liter sample of air at 25°C and 1.00 atm pressure was collected and dried. After drying, the volume of the sample was exactly 11.50 L. What was the percentage *by mass* of water in the original air sample?

    Answer: Under the conditions given, a mole of dry air occupies:

    22.4L×(298 K/273 K) = 24.5 L/mol

    mol dry air = 11.5L/(24.5 L/mol) = 0.469 mol

    The average molar mass of dry air is 29.1 g/mol

    The mass of dry air = 0.469 mol × 29.1 g/mol = 13.6 g

    mols of H_2O = 0.5L/(24.5 L/mol) = 0.0204 mol

    mass of H_2O = 0.0204 mol × 18.0 g/mol = 0.367 g

    % H_2O by mass = 100 × 0.367 g/(13.6 g + 0.367 g) = 2.62 %

12. The sunlight incident upon a 1 square meter area perpendicular to the line of transmission of the solar flux just above the Earth's atmosphere provides energy at a rate most closely equivalent to: (A) that required to power a pocket calculator, (B) that required to provide a moderate level of lighting for a 40-person capacity classroom illuminated with fluorescent lights, (C) that required to propel a 2500 pound automobile at 55 mph, (D) that required to power a 100-watt incandescent light bulb, (E) that required to heat a 40-person classroom to 70°F when the outside temperature is -10°F.

    Answer: (B) The solar flux of 1.34×10^3 watts per square meter would comfortably illuminate a medium-size classroom.

13. At an altitude of 50 km, the average atmospheric temperature is essentially 0°C. What is the average number of air molecules per cubic centimeter of air at this altitude?

    Answer: Solving the equation for P_h gives a pressure of 0.00190 atm. At this pressure and at 0°C, the volume of a mole of air is given by

$V = 22.4\ L/mol \times (1\ atm/0.00190\ atm) = 11{,}800\ L/mol = 1.18 \times 10^7\ cm^3/mol$

$(6.02 \times 10^{23}\ molecules/mol)/(1.18 \times 10^7\ cm^3/mol) = 5.10 \times 10^{16}\ molecules/cm^3$

14. What is the distinction between chemiluminescence and luminescence caused when light is absorbed by a molecule or atom?

    Answer: Both phenomena are emission of a photon from an excited species. In the case of chemiluminescence the excited species is the result of a chemical reaction whereas in the case of luminescence excitation is caused by absorption of a photon.

15. State two factors that make the stratosphere particularly important in terms of acting as a region where atmospheric trace contaminants are converted to other, chemically less reactive, forms.

    Answer: The stratosphere is exposed to intense ultraviolet radiation that causes photodissociation of molecules and generates species such as O atoms that can react with molecules. At lower altitudes in the troposphere this intense flux of ultraviolet radiation is not present. Few species reach the altitudes above the stratosphere where they could react.

16. What two chemical species are most generally responsible for the removal of hydroxyl radical from the unpolluted troposphere?

    Answer: Both CH_4 and CO react readily with hydroxyl radical resulting in its removal from the atmosphere.

17. What is the distinction between the symbols * and • in discussing chemically active species in the atmosphere?

    Answer: The symbol * denotes an excited state and • denotes a free radical with an unpaired electron

18. Of the following the true statement is (A) incoming solar energy is primarily in the form of infrared radiation, (B) The very cold tropopause layer at the top of the troposphere is the major absorber of harmful ultraviolet radiation from the sun, (C) The stratosphere is defined as a region of the atmosphere in which temperature decreases with increasing altitude, (D) a large fraction of solar energy is converted to latent heat by evaporation of water to produce water vapor in the atmosphere, (E) temperature inversions are most useful because they cause air pollutants to disperse.

    Answer: (D)

19. Of the following the true statement is (A) chemiluminescence refers to a chemical reaction that results from a molecule having absorbed a photon of light, (B) O* denotes an excited oxygen atom, (C) O_2* denotes a free radical, (D) HO• is an insignificant species in the atmosphere, (E) the longer the wavelength of incoming solar radiation, the more likely it is to cause a photochemical reaction to occur.

    Answer: (B)

20. Match the following pertaining to classes of atmospheric chemical species:

(A) NO_2	(1) Reductant
(B) H_2S	(2) Corrosive substance
(C) NH_4HSO_4	(3) Photochemically active species
(D) O_2*	(4) Of the species shown, most likely to dissociate without additional outside input

Answer: (A)-(3), (B)-(1), (C)-(2), (D)-(4)

21. Free radicals **do not** or **are not** (A) have unpaired electrons, (B) normally highly reactive, (C) last longer in the stratosphere than in the troposphere, (D) take part in chain reactions, (E) lose their energy spontaneously, reverting to a stable species by themselves.

    Answer: (E)

22. Of the following the true statement is (A) the central feature of global weather is the redistribution of moisture from equatorial areas where it falls to polar areas where it freezes, (B) cyclonic storms are caused by temperature inversions, (C) temperature inversions limit the vertical circulation of air, (D) albedo refers to the percentage of infrared radiation that is reabsorbed as energy is emitted from Earth, (E) the troposphere has a homogeneous composition of all gases and vapors including water.

    Answer: (C)

23. Using numbers ranging from 1 to 4, put the following in order of their anticipated lifetime in the troposphere from the shortest-lived (1) to the longest-lived (4) and explain: CH_4, CCl_2F_2, NO_2*, SO_2.

    Answer: (1) NO_2* because it is in an excited state and readily loses energy by emitting a photon, (2) SO_2 because it reacts to produce H_2SO_4 that can be washed from the atmosphere with precipitation, (3) CH_4 because it is a relatively stable molecule but does react with hydroxyl radical, (4) CCl_2F_2 is a notoriously stable molecule that does not react with hydroxyl radical and only breaks down when exposed to highly energetic ultraviolet radiation in the stratosphere.

24. Earth's atmosphere is stratified into layers. Of the following, the true statement regarding this stratification, the characteristics of the layers, and the characteristics of species in the layers is (A) the stratosphere and troposphere have essentially the same composition, (B) the upper boundary of the stratosphere is colder than the upper boundary of the troposphere because the former is higher, (C) ozone is most desirable near Earth's surface in the troposphere, (D) the composition of the troposphere is characterized by both its high and uniform content of water vapor, (E) the boundary between the troposphere and the stratosphere serves as a barrier to the movement of one of the important constituents of tropospheric air.

    Answer: (E)

Chapter 9
Particles in the Atmosphere

1. In 2006 the U.S. Environmental Protection Agency proposed lowering the allowable $PM_{2.5}$ level to 35 μg/m^3. How many particles would this be in a cubic meter of air assuming that all the particles were spheres of a diameter of 2.5 μm and had a density of exactly 1 g/cm^3?

   Answer: From the formula for the volume of a sphere, calculate the volume of each sphere. From the density given, calculate the mass of each sphere and divide this number into 35 μg to get the number of spheres.

   The volume of 1 sphere, $V = 4/3\ \pi r^3 = 4/3 \times 3.14 \times (1.25\ \mu m)^3 = 8.18\ \mu m^3$

   Density of particles = $(1 \times 10^6\ \mu g)/(1 \times 10^{12}\ \mu m^3) = 1 \times 10^{-6}\ \mu g/\mu m^3$

   Mass of 1 particle = $8.18\ \mu m^3$/particle $\times\ 1 \times 10^{-6}\ \mu g/\mu m^3 = 8.18 \times 10^{-6}\ \mu g$/particle

   Total particles in 1 m^3 = $35\ \mu g/(8.18 \times 10^{-6}\ \mu g$/particle$) = 4.28 \times 10^6$ particles/m^3

2. For small charged particles, those that are 0.1 μm or less in size, an average charge of 4.77×10^{-10} esu is normally assumed for the whole particle. What is the surface charge in esu/cm^2 for a charged spherical particle with a radius of 0.1 μm?

   Answer: Substituting $r = 1 \times 10^{-5}$ cm into the formula for the area of the surface of a sphere, $4\pi r^2$, gives a surface area of 1.26×10^{-9} cm^2 for the spherical particle. Therefore, the surface charge in esu/cm^2 is

   Charge = $(4.77 \times 10^{-10}$ esu$)/(1.26 \times 10^{-9}$ cm$^2) = 0.379$ esu/cm^2

3. What is the settling velocity of a particle having a Stokes' diameter of 10 μm and a density of 1 g/cm^3 in air at 1.00 atm pressure and 0°C temperature? (The viscosity of air at 0°C is 170.8 micropoise. The density of air under these conditions is 1.29 g/L.)

   Answer: Substitute into Stokes' law equation:

   $$v = \frac{gd^2(\rho_1 - \rho_2)}{18\eta}$$

   where v is the settling velocity in cm/sec; g is the acceleration of gravity, 981 cm/sec^2; ρ_1 is the density of the particle, 1 g/cm^3; ρ_2 is the density of air 1.29×10^{-3} g/cm^3; and η is the viscosity of air, 1.71×10^{-4} poise, $v = 5.7 \times 10^{-3}$ cm/sec.

4. A freight train that included a tank car containing anhydrous NH_3 and one containing concentrated HCl was wrecked, causing both of the tank cars to leak. In the region between the cars a white aerosol formed. What was it, and how was it produced?

   Answer: The white aerosol was solid NH_4Cl formed by the reaction:

   $NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$

5. Examination of aerosol fume particles produced by a welding process showed that 2% of the particles were greater than 7 μm in diameter and only 2% were less than 0.5 μm. What is the mass median diameter of the particles?

   Answer: Using Figure 9.3, place a point at 7 μm/98% and another at 0.5 μm/2%; draw a straight line between them; and read the diameter at 50%, which gives a value of 2.0 μm

for the mass median diameter of the particles.

6. What two vapor forms of mercury might be found in the atmosphere?

   Answer: Elemental mercury and dimethyl mercury

7. Analysis of particulate matter collected in the atmosphere near a seashore shows considerably more Na than Cl on a molar basis. What does this indicate?

   Answer: The particles were originally NaCl from evaporation of water from ocean spray droplets. Reaction with H_2SO_4 in the atmosphere would have caused some of the Cl to be lost as HCl vapor and be replaced by SO_4.

8. What type of process results in the formation of very small aerosol particles?

   Answer: Very small particles tend to be condensation aerosols formed by reactions of gases.

9. Which size range encompasses most of the particulate matter mass in the atmosphere?

   Answer: Atmospheric particles generally fall within the range of 0.01 μm to around 100 μm. The total mass of atmospheric particles is concentrated in the larger size range whereas the total number and surface area of atmospheric particles is in the smaller fraction.

10. Why are aerosols in the 0.1–1 μm size range especially effective in scattering light?

    Answer: These particles are of about the same dimensions as the wavelengths of visible light which makes them especially effective in scattering light.

11. Per unit mass, why are smaller particles relatively more effective catalysts for atmospheric chemical reactions?

    Answer: The smaller particles are relatively much more numerous and have greater total surface areas on which reactions may be catalyzed.

12. In terms of origin, what are the three major categories of elements found in atmospheric particles?

    Answer: As seen in Figure 9.4, the three major categories of elements found in atmospheric particles are; elements from natural sources, elements largely introduced by human activities, and materials formed by atmospheric reactions.

13. What are the five major classes of material making up the composition of atmospheric aerosol particles?

    Answer: The answer does not need to be confined to five choices; reasonable ones are oxides (ash, such as fly ash), salts, water, organic substances, and carbon (soot). Others that should be mentioned include soil and sulfuric acid (in acid droplets).

14. The size distribution of particles emitted from coal-fired power plants is bimodal. What are some of the properties of the smaller fraction in terms of potential environmental implications?

    Answer: The smaller particle fraction includes the greater number of particles, the higher surface area, the particles most difficult to remove, and those that are most respirable into the lungs.

15. Of the following, the statement that is **untrue** regarding particles in the atmosphere is (explain): (A) Dispersion aerosol particles formed by grinding up bulk matter are typically relatively large, (B) very small particles tend to be acidic and often originate from gases, (C) Al, Fe, Ca, and Si in particles often come from soil erosion, (D)

carcinogenic polycyclic aromatic hydrocarbons may be synthesized from saturated hydrocarbons under oxygen-deficient conditions, (E) larger particles are more harmful because they contain more matter.

Answer: (E) is untrue, larger particles are relatively less harmful because they are less respirable and damaging to the lungs.

16. Of the following, the species that is **least likely** to be a constituent of solid or liquid atmospheric particulate matter is (explain): (A) C, (B) O_3 (C) H_2SO_4, (D) NaCl, (E) benzo(a)pyrene.

Answer: (B) O_3 would not be in particles because it is a gas.

17. Of the following, the one that is **not** a characteristic of dispersion aerosols is (explain): (A) They are most readily carried into the alveoli of lungs, (B) they are usually above 1 μm in size, (C) they are relatively easier to remove, (D) they are generally less respirable, (E) they are produced when bulk materials (larger particles) are ground up or sub-divided.

Answer: (A), dispersion aerosols tend to be relatively large and not carried readily into the lungs.

18. Match the constituent of particulate matter from the left with its most likely source from the right, below:

(A) Si (1) Natural sources, soil erosion

(B) PAH (2) Incomplete combustion of hydrocarbons

(C) SO_3^{2-} (3). Element largely introduced by human activities

(D) Pb (4) Reaction of a gas in the atmosphere

Answer: (A)-(1), (B)-(2), (C)-(4), (D)-(3)

19. Of the following, the most likely to be formed by pyrosynthesis is (explain): (A) Sulfate particles, (B) Ammonium particles, (C) sulfuric acid mist, (D) PAHs, (E) ozone in smog.

Answer: (D)

20. Match each particle constituent below, left, with its likely source:

(A) Si (1) From gases in the surrounding atmosphere

(B) V (2) From natural sources

(C) Benzo(a)pyrene (3) Combustion of certain kinds of fuel oil

(D) Sulfuric acid droplets (4) From incomplete combustion

Answer: (A)-2, (B)-3, (C)-4, (D)-1

Chapter 10
Gaseous Inorganic Air Pollutants

1. Why is it that "highest levels of carbon monoxide tend to occur in congested urban areas at times when the maximum number of people are exposed?"

   Answer: Carbon monoxide comes primarily from automobile exhausts and levels are especially high in areas of heavy traffic such as busy intersections.

2. Which unstable, reactive species is responsible for the removal of CO from the atmosphere?

   Answer: The hydroxyl radical, HO•, reacts rapidly with CO resulting in its oxidation to CO_2.

3. Which of the following fluxes in the atmospheric sulfur cycle is smallest: (A) sulfur species washed out in rainfall over land, (B) sulfates entering the atmosphere as "sea salt," (C) sulfur species entering the atmosphere from volcanoes, (D) sulfur species entering the atmosphere from fossil fuels, (E) hydrogen sulfide entering the atmosphere from biological processes in coastal areas and on land?

   Answer: The correct answer is (B) because "sea salt" is predominantly NaCl without much sulfate, although subsequent atmospheric reactions involving SO_2 and its reaction products can convert some of the NaCl to Na_2SO_4 in particles.

4. Of the following agents, the one that would not favor conversion of sulfur dioxide to sulfate species in the atmosphere is: (A) ammonia, (B) water, (C) contaminant reducing agents, (D) ions of transition metals such as manganese, (E) sunlight.

   Answer: The correct answer is (C) because reductants would tend to prevent sulfur dioxide from being converted to sulfate.

5. Of the stack gas scrubber processes discussed in this chapter, which is the least efficient for the removal of SO_2?

   Answer: Injection of dry powdered limestone ($CaCO_3$) into stack gas is relatively ineffective in removing SO_2.

6. The air inside a garage was found to contain 10 ppm CO by volume at standard temperature and pressure (STP). What is the concentration of CO in mg/L and in ppm by mass?

   Answer: Using 29.0 g/mol as the average mass of a mol of air in the troposphere, 22.4 L of air has a mass of 29.0 g. If the air is 10 parts per million CO there is 1.00×10^{-5} mol of CO in 22.4 L of air giving:

   Mass CO = 1.00×10^{-5} mol × 28.0 g/mol = 2.8×10^{-4} g CO = 0.28 mg CO

   mg/L CO = 0.28 mg/22.4 L = 0.0125 mg/L

   ppm mass CO = $10^6 \times 2.8 \times 10^{-4}$ g/29 g = 9.7 ppm

7. How many metric tons of 5%–S coal would be needed to yield the H_2SO_4 required to produce a 3.00–cm rainfall of pH 2.00 over a 100 km^2 area?

   Answer: Given 1×10^6 m^2/km^2, the volume of the rainfall is given by

$V = 3.00 \times 10^{-2}$ m $\times$ 100 km^2 $\times$ 1×10^6 m^2/km^2 = 3.00×10^6 m^3

In liters V = 3.00×10^6 m^3 $\times$ 1×10^3 L/m^3 = 3.00×10^9 L

At pH 2.0, mol H^+ = 3.00×10^9 L $\times$ 1.00×10^{-2} mol/L = 3.00×10^7 mol H^+

Since each mol of H_2SO_4 yields 2 mol H^+, mole H_2SO_4 = $0.5 \times 3.00 \times 10^7 = 1.50 \times 10^7$ mol. That number of moles of H_2SO_4 would come from 1.50×10^7 mol S.

Mass S = 1.50×10^7 mol $\times$ 32.0 g/mol S = 4.8×10^8 g S or 480 tonne S (tonne = metric ton)

Mass coal required = 480 tonne/0.05 = 9,600 tonne coal

8. In what major respect is NO_2 a more significant species than SO_2 in terms of participation in atmospheric chemical reactions?

   Answer: NO_2 can undergo photochemical dissociation to yield reactive O atoms that start atmospheric chain reactions.

9. Assume that an incorrectly adjusted lawn mower is operated in a garage such that the combustion reaction in the engine is

   $C_8H_{18} + {}^{17}/_2O_2 \rightarrow 8CO + 9H_2O$

   If the dimensions of the garage are 5 $\times$ 3 $\times$ 3 meters, how many grams of gasoline must be burned to raise the level of CO in the air to 1000 ppm by volume at STP?

   Answer: The volume of air in the garage is 45 m^3 = 4.5×10^4 L

   Mol air = 4.5×10^4 L/22.4 L/mol = 2.01×10^3 mol

   Since 1000 ppm is 1 part per thousand, there are 2.01 mol CO in it

   At a mole ratio of 1 mol C_8H_{18}/8 mol CO,

   Mol C_8H_{18} = 1/8 $\times$ 2.01 = 0.251 mol C_8H_{18}

   Mass C_8H_{18} = 0.251 mol C_8H_{18} $\times$ 114 g/mol = 28.6 g C_8H_{18}

10. A 12.0-L sample of waste air from a smelter process was collected at 25°C and 1.00 atm pressure, and the sulfur dioxide was removed. After SO_2 removal, the volume of the air sample was 11.50 L. What was the percentage by mass of SO_2 in the original sample?

    Answer: Under the conditions given, a mole of air occupies:

    22.4L$\times$(298 K/273 K) = 24.5 L/mol

    Mol of air in 12.0 L air = 12.0 L/(24.5 L/mol) = 0.490 mol

    Of this air, 0.50 L/(24.5 L/mol) = 0.0204 mol SO_2

    Using 29.1 g/mol for the molar mass of uncontaminated air

    Mass of 0.490 mol "pure" air = 0.490 mol $\times$ 29.1 g/mol = 13.6 g

    Mol of SO_2 = 0.5L/(24.5 L/mol) = 0.0204 mol

    Mass of SO_2 = 0.0204 mol $\times$ 64.0 g/mol = 1.31 g

    % SO_2 by mass = 100 $\times$ 1.31 g/(13.6 g + 1.31 g) = 8.8% SO_2

11. What is the oxidant in the Claus reaction? What is the commercial product of this reaction?

    Answer: SO_2 is the oxidant in the reaction $2H_2S + SO_2 \rightarrow 3S + 2H_2O$ Elemental sulfur is produced as a commercial product.

12. Carbon monoxide is present at a level of 10 ppm by volume in an air sample taken at 15°C and 1.00 atm pressure. At what temperature (at 1.00 atm pressure) would the sample also contain 10 mg/m^3 of CO?

    Answer: A mole of air at 15°C and 1.00 atm pressure has a volume of

    V = 22.4 L × (288K/273K) = 23.6 L

    Mol CO in 23.6 L air = 1.00×10^{-5} mol

    Mass CO = 1.00×10^{-5} mol × 28.0 g/mol = 2.8×10^{-4} g CO = 0.28 mg CO

    Given 1000 L/m^3, the volume of air at 15°C and 1.00 atm containing 10 mg CO is

    V_{air} = 23.6 L × (10 mg/L)/(0.28 mg/L) = 843 L

    The temperature at which this amount of air would occupy 1000 L at 1.00 atm P is

    T = 288 K × (1000L/843 L) = 342 K = 69°C

13. How many metric tons of coal containing an average of 2% S are required to produce the SO_2 emitted by fossil fuel combustion shown in Figure 10.1? (Note that the values given in the figure are in terms of elemental sulfur, S.) How many metric tons of SO_2 are emitted? How does this amount of coal compare to that currently used in the world?

    Answer: 100 million tonne/0.02 = 5.0 billion tonne of coal

    Mass SO_2 = 100 million tonne × (64 tonne /32 tonne S) = 200 million tonne SO_2

14. Assume that the wet limestone process requires 1 metric ton of $CaCO_3$ to remove 90% of the sulfur from 4 metric tons of coal containing 2% S. Assume that the sulfur product is $CaSO_4$. Calculate the percentage of the limestone converted to calcium sulfate.

    Answer: The mass of sulfur removed from 4 tonne coal is given by

    Mass S = 4.00 tonne × 0.90 × 0.02 = 0.072 tonne S (atomic mass 32)

    If this is converted to $CaSO_4$, from $CaCO_3$, molar mass 100 g/mol

    Mass $CaCO_3$ converted = 0.072 tonne S × (100 g $CaCO_3$/32 g S) = 0.225 tonne $CaCO_3$

    % $CaCO_3$ converted = 100 × (0.225 tonne/1 tonne) = 22.5%

15. Referring to the two preceding problems, calculate the number of metric tons of $CaCO_3$ required each year to remove 90% of the sulfur from 1 billion metric tons of coal (approximate annual U.S. consumption), assuming an average of 2% sulfur in the coal.

    Answer: Each 4 metric tons of coal requires 1 metric ton of $CaCO_3$, so 250 million metric tons of $CaCO_3$ would be required.

16. If a power plant burning 10,000 metric tons of coal per day with 10% excess air emits stack gas containing 100 ppm by volume of NO, what is the daily output of NO? Assume the coal is pure carbon.

    Answer: Assume air is 21% O_2 and is at STP (273 K, 1.00 atm)

    From the stoichiometry of the reaction $C + O_2 \rightarrow CO_2$, the mass of O_2 needed is given by:

    Mass O_2 = 10,000 tonne × (32 tonne O_2/12 tonne C) = 2.67×10^4 tonne O_2

    Stoichiometric mass air = 2.67×10^4 tonne/0.21 = 1.27×10^5 tonne air = 1.27 ×

10^{11} g air

To account for 10% excess air,

Mass air = 1.27×10^5 tonne $\times$ 1.10 = 1.40×10^5 tonne air = 1.40×10^{11} g air

Using 1.29 g/L for the density of air, its volume is given by

V = 1.40×10^{11} g/1.29 g/L = 1.09×10^{11} L

Mol air = 1.09×10^{11} L/(22.4 L/mol) = 4.84×10^9 mol air

At 100 ppm NO, the mol fraction of NO is 1.00×10^{-4}

Mol NO = 1.00×10^{-4} mol NO/mol air $\times$ 4.84×10^9 mol air = 4.84×10^5 mol NO

Mass NO = 4.84×10^5 mol NO $\times$ 30.0 g NO/mol NO = 1.45×10^7 g NO

The daily output of NO is 14.5 tonne/day

17. How many cubic kilometers of air at 25°C and 1 atm pressure would be contaminated to a level of 0.5 ppm NO_x from the power plant discussed in the preceding question?

    Answer: At 25°C and 1.00 atm the molar volume of air is 24.5 L/mol and at 0.5 ppm NO the number of mol NO in a molar volume of air is 5×10^{-7} mol. In the preceding problem the number of mol NO produced per day was 4.84×10^5 mol NO so the volume of air contaminated in a day is given by

    V = 4.84×10^5 mol NO $\times$ 24.5 L air/mol air/(5×10^{-7} mol NO/mol air) = 2.37×10^{13} L air

    V_{air} in km^3 = 2.37×10^{13} L $\times$ 1.00×10^{-3} m^3/L $\times$ 1.00×10^{-9} km^3/m^3 = 23.7 km^3

18. Match the following pertaining to gaseous inorganic air pollutants:

    (A) CO, (B) O_3, (C) SO_2, (D) NO

    (1) Produced in internal combustion engines as a precursor to photochemical smog formation

    (2) Formed in connection with photochemical smog

    (3) Not associated particularly with smog or acid rain formation, but of concern because of its direct toxic effects

    (4) Does not cause smog to form, but is a precursor to acid rain.

    Answer: (A)-(3), (B)-(2), (C)-(4), (D)-(1)

19. Of the following, the one that is **not** an inorganic pollutant gas is (explain): (A) Benzo(a)pyrene, (B) SO_2, (C) NO, (D) NO_2, (E) H_2S.

    Answer: (A) Benzo(a)pyrene is a carbon-rich hydrocarbon

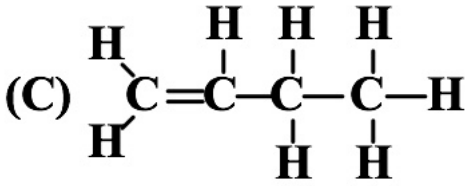
20. Of the following, the statement that is **not** true regarding carbon monoxide in the atmosphere is (explain): (A) It is produced in the stratosphere by a process that starts with H abstraction from CH_4 by HO•, (B) it is removed from the atmosphere largely by reaction with hydroxyl radical, (C) it is removed from the atmosphere in part by its being metabolized by soil microorganisms, (D) it has some natural, as well as pollutant, sources, (E) at its average concentration in the global atmosphere, it is probably a threat to human health.

    Answer: (E) Carbon monoxide is a health hazard only in localized areas of high concentration

Chapter 11
Organic Air Pollutants

1. Match each organic pollutant designated with a letter in the top list with its expected effect in the numbered bottom list, below:

   (A) CH_3SH (B) $CH_3CH_2CH_2CH_3$

   (C) 

   (1) Most likely to have a secondary effect in the atmosphere (2) Most likely to have a direct effect (3) Should have the least effect of these three

   Answer: (A)-(2), (B)-(3), (C)-(1)

2. Why are hydrocarbon emissions from uncontrolled automobile exhaust particularly reactive?

   Answer: Because they have a high concentration of reactive alkenes

3. Assume an accidental release of a mixture of gaseous alkanes and alkenes into an urban atmosphere early in the morning. Assume that the mass of air is subjected to intense sunlight during the day and is kept in a stagnant condition by a thermal inversion. If the atmosphere at the release site is monitored for these compounds, what can be said about their total and relative concentrations at the end of the day? Explain.

   Answer: The conditions described are those in which photochemical smog forms. The concentrations of both kinds of hydrocarbons should decrease during the day as they undergo reactions with O atoms, HO• radicals, and O_3. The concentrations of the more reactive alkenes would decrease faster than those of the alkanes and the ratio of alkanes to alkenes would increase during the day.

4. Match each radical in the top column with its type in the lower column, below:

   (A) H_3C• (B) CH_3CH_2O• (C) $CH_xCH_{2x+1}O_2$• (D) $\mathbf{H\dot{C}O}$

   (1) Formyl radical (2) Alkylperoxyl radical (3) Alkyl radical (4) Alkoxyl radical

   Answer: (A)-3, (B)-4, (C)-2, (D)-1

5. When reacting with hydroxyl radical, alkenes have a reaction mechanism not available to alkanes, which makes the alkenes much more reactive. What is this mechanism?

   Answer: Alkenes can undergo addition reactions, which are particularly rapid with hydroxyl radical.

6. What is the most stable type of hydrocarbon that has a very low hydrogen-to-carbon ratio?

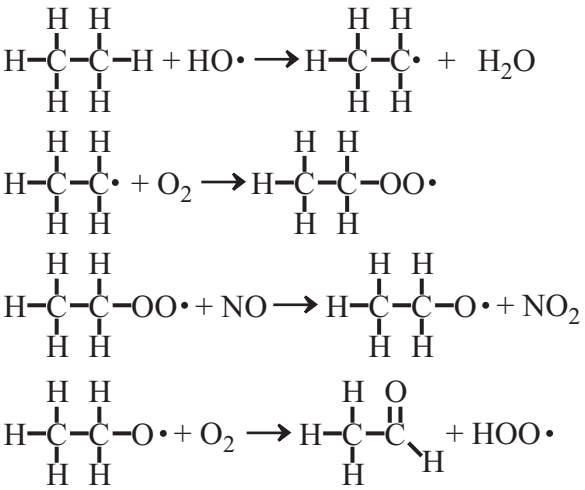
   Answer: Polycyclic aromatic hydrocarbons such as benzo(a)pyrene

7. In the sequence of reactions leading to the oxidation of hydrocarbons in the atmosphere, what is the first stable class of compounds generally produced?

   Answer: Carbonyl compounds, the aldehydes and ketones

8. Give a sequence of reactions leading to the formation of acetaldehyde from ethane starting with the reaction of hydroxyl radical.

   Answer:



9. What important photochemical property do carbonyl compounds share with NO_2?

   Answer: The ability to become excited species by absorption of relatively long-wavelength (low energy) ultraviolet radiation.

10. Of the following, the statement that is **untrue** regarding air pollutant hydrocarbons is (explain): (A) Although methane, CH_4, is normally considered as coming from natural sources, and may be thought of as a non-pollutant, human activities have increased atmospheric methane levels, with the potential for doing harm, (B) some organic species from trees can result in the formation of secondary pollutants in the atmosphere, (C) alkenyl hydrocarbons containing the C=C group have a means of reacting with hydroxyl radical that is not available for alkanes (D) the reactivities of individual hydrocarbons as commonly measured for their potential to form smog, vary only about ±25% (E) most non-methane hydrocarbons in the atmosphere are of concern because of their ability to produce secondary pollutants.

    Answer: (D) is untrue. Hydrocarbon reactivities to form photochemical smog vary over several orders of magnitude.

11. Of the following regarding organic air pollutants, the true statement is (explain): (A) Carbonyl compounds (aldehydes and ketones) are usually the last organic species formed during the photochemical oxidation of hydrocarbons, (B) carboxylic acids (containing the $-CO_2H$ group) are especially long-lived and persistent in the atmosphere, (C) chlorofluorocarbons, such as CCl_2F_2, are secondary pollutants, (D) peroxyacetyl nitrate, PAN, is a primary pollutant, (E) HFCs pose a greater danger to the stratospheric ozone layer than do CFCs.

    Answer: None of these choices would be correct. (A) could be a plausible choice because in the sense that the carbonyl compounds form as the first semi-stable species produced in the smog-forming process, although they tend to react further to form more stable species such as carboxylic acids.

12. Of the following, the true statement regarding atmospheric hydrocarbons is (explain): (A) alkanes readily undergo addition reactions with hydroxyl radicals, (B) alkenes undergo addition reactions with hydroxyl radical, (C) ozone tends to add across C-H bonds in alkanes,

(D) hydrocarbons tend to be formed by the chemical reduction of esters evolved by plants, (E) unsaturated alkenes tend to be evolved from evaporation of gasoline, whereas alkanes are produced as automotive exhaust products.

Answer: (B) is correct because hydroxyl radical readily adds across the double bonds in alkenes to produce oxygenated hydrocarbon radicals.

13. Of the following, the **untrue** statement pertaining to hydrocarbons in the atmosphere is (explain): (A) hydrocarbons generated and released by human activities constitute only about 1/7 of the total hydrocarbons in the atmosphere, (B) natural sources are the most important contributors of organics in the atmosphere, (C) the reaction $2\{CH_2O\}$(bacterial action) $\rightarrow CO_2\ (g) + CH_4(g)$ is a huge contributor to atmospheric hydrocarbons, (D) methane, CH_4, is produced by a variety of plants and released to the atmosphere, (E) a number of plants evolve a simple hydrocarbon that is highly reactive with hydroxyl radical, HO•, and with oxidizing species in the atmosphere.

Answer: Based upon information in the text, (D) would be regarded as untrue because it was believed that methane is generated by bacteria in the biosphere, but generally not from plants. However, relatively recent (2014) investigations have suggested that methane is produced from the sulfur-containing amino acid methionine by some plants.

14. An important characteristic of atmospheric carbonyl compounds is (explain): (A) Aldehydes are second only to NO_2 as atmospheric sources of free radicals produced by the absorption of light because the carbonyl group is a **chromophore**, (B) they are normally the final products of oxidation of atmospheric hydrocarbons, and are relatively harmless in the atmosphere, (C) they are free radicals with unpaired electrons, (D) they are the predominant organic compounds emitted from auto exhausts, (E) alkenyl) aldehydes such as acrolein are especially stable and unreactive in the atmosphere.

Answer: (A) is the correct answer because the carbonyl group is a chromophore that can absorb ultraviolet radiation leading to free radical formation.

Chapter 12
Photochemical Smog

1. Of the following species, the one which is the least likely product of the absorption of a photon of light by a molecule of NO_2 is: (A) O, (B) a free radical species, (C) NO, (D) NO_2*, (E) N atoms.

   Answer: (E)

2. Which of the following statements is true: (A) RO• reacts with NO to form alkyl nitrates, (B) RO• is a free radical, (C) RO• is not a very reactive species, (D) RO• is readily formed by the action of stable hydrocarbons and ground state NO_2, (E) RO• is not thought to be an intermediate in the smog-forming process.

   Answer: (B)

3. Of the following species, the one most likely to be found in reducing smog is: ozone, relatively high levels of atomic oxygen, SO_2, PAN, PBN.

   Answer: SO_2

4. Why are automotive exhaust pollutant hydrocarbons even more damaging to the environment than their quantities would indicate?

   Answer: Automotive exhaust pollutant hydrocarbons contain a relatively high proportion of unsaturated alkenes, which readily react in the atmosphere to produce photochemical smog.

5. At what point in the smog-producing chain reaction is PAN formed?

   Answer: PAN is generated as the result of several chain reactions near the end of the smog-forming process.

6. Of the smog products mentioned in this chapter, which particularly irritating product is likely to be formed in the laboratory by the irradiation of a mixture of benzaldehyde and NO_2 with ultraviolet light?

   Answer: The product would be peroxybenzoyl nitrate (PBN), a powerful irritant and tear-producing agent.

7. Which of the following species reaches its peak value last on a smog-forming day: NO, oxidants, hydrocarbons, NO_2?

   Answer: Oxidants

8. What is the main species responsible for the oxidation of NO to NO_2 in a smoggy atmosphere?

   Answer: Organic peroxy radicals, ROO•, oxidize NO to NO_2 in a smoggy atmosphere.

9. Give reasons why a turbine engine should have lower hydrocarbon emissions than an internal combustion engine.

   Answer: Lack of wall quench because of uniformly hot surfaces and presence of excess air should lead to a turbine engine having lower hydrocarbon emissions than a piston internal combustion engine.

10. What pollution problem does a lean mixture aggravate when employed to control hydrocarbon emissions from an internal combustion engine?

Answer: A lean mixture tends to produce more nitrogen oxides.

11. Why is a modern automotive catalytic converter called a "three-way conversion catalyst?"

    Answer: It is called a three-way conversion catalyst because a single catalytic unit destroys all three of the main classes of automobile exhaust pollutants — hydrocarbons, carbon monoxide, and nitrogen oxides.

12. What is the distinction between *reactivity* and *instability* as applied to some of the chemically active species in a smog-forming atmosphere?

    Answer: A reactive species has a strong tendency to react but, in the absence of some species with which to react, it might be relatively stable. An unstable species is one that tends to gain stability by undergoing some sort of process on its own. Sulfur dioxide, SO_2, is stable for some time in the atmosphere in the absence of oxidants such as those present in photochemical smog in which case it undergoes rapid oxidation. Excited nitrogen dioxide, NO_2*, is unstable and readily emits a photon to revert to ground-state NO_2.

13. Why might carbon monoxide be chosen as a standard against which to compare automotive hydrocarbon emissions in atmospheres where smog is formed? What are some pitfalls created by this choice?

    Answer: CO in the atmosphere is indicative of automobile exhaust pollution. However, it is oxidized rather readily in the presence of photochemical smog, which might make it an unreliable measure of hydrocarbon emissions.

14. What is the purpose of alumina in an automotive exhaust catalyst? What kind of material actually catalyzes the destruction of pollutants in the catalyst?

    Answer: Alumina is the solid, porous catalyst support. The actual catalytic material consists of precious metals coated in a very thin layer on the alumina support.

15. Some atmospheric chemical reactions are abstraction reactions and others are addition reactions. Which of these applies to the reaction of hydroxyl radical with propane? With propene (propylene)?

    Answer: Propane would have to undergo an abstraction reaction, such as removal of an H atom by reaction with an O atom. Propene can also undergo abstraction reactions, but is more likely to undergo addition, particularly with HO• adding across a double bond.

16. How might oxidants be detected in the atmosphere?

    Answer: The classical means of detecting oxidants in the atmosphere is oxidation of I^- to I_3^-.

17. Each of the following occurs during smog formation. Place each in order from the one that occurs first (denoted 1) to the one that occurs last (denoted 5) and explain your choice: (A) An alkyl peroxyl radical, ROO•, is produced, (B) particles in the atmosphere obscure visibility, (C) NO and another product are produced from NO_2, (D) NO reacts to produce NO_2, (E) an alkyl radical, R•, is produced from a hydrocarbon.

    Answer: The order would be 1-C, 2-E, 3-A, 4-D, 5-B. The process is initiated by the photochemical dissociation of NO_2 to produce O atoms. The O atoms extract H from hydrocarbons to yield alkyl radicals, R•, which in turn add O_2 to produce peroxyl radicals, ROO•. NO_2 is regenerated by the oxidation of NO by ROO•. The last step in the process is the generation of particles as the final products of the photochemical oxidation of organics in the atmosphere.

18. Why is ozone especially damaging to rubber?

    Answer: Ozone is especially damaging to rubber because of its strong tendency to add across

double bonds in the rubber polymer causing the rubber to become brittle.

19. Show how hydroxyl radical, HO•, might react differently with ethylene, $H_2C=CH_2$, and methane, CH_4.

    Answer: HO• adds across the double bond in $H_2C=CH_2$ to produce an oxygenated free radical, $H_3C\text{-}CH_2O$•. The hydroxyl radical abstracts a hydrogen atom from CH_4 to produce a methyl radical, H_2C•.

20. Name the stable product that results from an initial addition reaction of hydroxyl radical, HO•, with benzene.

    Answer: Phenol can be the end product of the addition of HO• to benzene.

21. Of the following, the true statement is (explain): (A) NO_2 is **not** involved in the processes that initiate smog formation, only in those that tend to stop it, (B) NO undergoes photodissociation to start the process of smog formation, (C) NO_2 can react with free radical species to terminate chain reactions involved in smog formation, (D) once NO_2 has undergone photodissociation, there is not a mechanism in a smog-forming atmosphere by which it can be regenerated, (E) NO_2 is the most phytotoxic (toxic to plants) species present in a smoggy atmosphere.

    Answer: (C) because the NO_2 molecule has an unpaired electron and can react with free radicals and stop chain reactions.

22. Of the following, the statement that is **untrue** regarding air pollutant hydrocarbons is (explain): (A) Although methane, CH_4, is normally considered as coming from natural sources, and may be thought of as a non-pollutant, human activities have increased atmospheric methane levels, with the potential for doing harm, (B) some organic species from trees can result in the formation of secondary pollutants in the atmosphere, (C) alkenyl hydrocarbons containing the C=C group have a means of reacting with hydroxyl radical that is not available for alkanes, (D) the reactivities of individual hydrocarbons as commonly measured for their potential to form smog, vary only about ±25%, (E) most non-methane hydrocarbons in the atmosphere are of concern because of their ability to produce secondary pollutants.

    Answer: (D) is incorrect because the reactivities of hydrocarbons as measured by the rates of their reactions with hydroxyl radical can vary over several orders of magnitude.

23. Of the following, the true statement pertaining to hydrocarbon reactivity in smog formation is (explain): (A) Alkanes are more reactive than alkenes (olefins), (B) reactivity is based on reaction with HO•, (C) methane, CH_4, is the most reactive hydrocarbon, (D) terpenes, such as *d*-limonene, are unreactive, (E) hydroxyl radical is classified as an unreactive hydrocarbon.

    Answer: (B) is the correct answer because rates of reaction with hydroxyl radical are used to express reactivities.

24. Smog aerosol droplets are composed of organic matter surrounding a small inorganic (mineral matter) core. Suggest what this shows regarding the process by which these aerosols are formed. Is the organic portion of the aerosol likely to be pure hydrocarbon (explain)?

    Answer: This phenomenon probably indicates that small inorganic particles serve as condensation nuclei around which organic molecules formed in smog condense. The organic portion of the aerosol would not be hydrocarbon, but would consist of oxygenated organic species generated by the oxidizing conditions in photochemical smog.

Chapter 13
The Endangered Global Atmosphere

1. How do modern transportation practices contribute to the kinds of atmospheric problems discussed in this chapter?

   Answer: The internal combustion engine used in automobiles, trucks, train locomotives, and (as gas turbines) aircraft emits carbon dioxide gas to the atmosphere, which causes global warming, and also emits reactive hydrocarbons and nitrogen oxides, which are ingredients of photochemical smog.

2. What is the rationale for classifying most acid rain as a secondary pollutant?

   Answer: The major acid rain constituents are formed as secondary products of non-acidic gases (NO that produces HNO_3) or weakly acidic gases (SO_2 that gets oxidized to strong acid H_2SO_4).

3. Distinguish among UV-A, UV-B, and UV-C radiation. Why does UV-B pose the greatest danger in the troposphere?

   Answer: UV-A radiation has a wavelength in the range 320 nm-400 nm and, because of its relatively low energy, is less harmful to exposed organisms; UV-B radiation, 290 nm < λ < 320 nm, penetrates into the troposphere and is very damaging to tissue; whereas UV-C radiation, λ < 290 nm, does not penetrate to the troposphere.

4. How does the extreme cold of stratospheric clouds in Antarctic regions contribute to the Antarctic ozone hole?

   Answer: These clouds consist largely of small ice crystals which, over the winter months accumulate reactive Cl-containing species. Warming of the clouds and exposure to ultraviolet radiation in the Antarctic spring releases a "burst" of ozone-destroying reactive Cl species.

5. How does the oxidizing nature of ozone from smog contribute to the damage that it does to cell membranes?

   Answer: Ozone attacks unsaturated bonds in fatty acid constituents of cell membranes.

6. What may be said about the time and place of the occurrence of maximum ozone levels from smog with respect to the origin of the primary pollutants that result in smog formation?

   Answer: Maximum ozone levels tend to occur downwind and at a later time compared to the location and time of entry of the smog precursors into the atmosphere.

7. What is the basis for "nuclear winter"?

   Answer: Blasting huge amounts of smoke and particulate matter very high into the atmosphere due to nuclear explosions such that it blocks out sunlight, causing severe cooling. Stratospheric ozone would also be destroyed.

8. Discuss the analogies between the effects of a large asteroid hit on Earth with "nuclear winter."

   Answer: A large asteroid hit would cause much the same effects as those from "nuclear winter," blasting huge amounts of particulate matter into the atmosphere and destroying the

protective stratospheric ozone layer. The extent of these effects would depend upon the relative magnitude of a nuclear blast event and the size of the asteroid. It is difficult to imagine a scenario in which a nuclear war would cause such catastrophic global effects as would the impact of a very large asteroid, such as those that have caused mass extinctions of species millions of years ago.

9. What is meant by a "tie-in strategy"?

   Answer: Such a strategy is one in which measures taken to alleviate a destructive pollution phenomenon would be beneficial in other ways, such as conservation of resources. A good example is the replacement of fuel-consuming modes of transportation by those that use renewable resources, such as electrified railways using wind-generated electricity.

10. Of the following, the statement that is **untrue** is (explain): (A) Acid rain is denoted by any precipitation with a pH less than neutral (7.00), (B) acid may be deposited as acidic salts and acid gases, in addition to aqueous acids, (C) acid rain is a regional air pollution problem as distinguished from local or global problems, (D) carbon dioxide makes rainfall slightly acidic, (E) acid rain is often associated with elevated levels of sulfate ion, SO_4^{2-}.

    Answer: (A) is untrue because unpolluted rainwater has a pH of somewhat less than 7 due to the presence of CO_2, which is present in the atmosphere naturally (though excessive levels can be considered to be polluting).

11. Of the following related to greenhouse gases and global warming, the true statement is (explain): (A) levels of greenhouse gas methane are increasing by about 1 ppm per year in the atmosphere, (B) per molecule, methane has a greater effect on greenhouse warming than does carbon dioxide, (C) radiative forcing of CO_2 is about 25 times that of CH_4, (D) carbon dioxide is the only gas considered significant as a cause of greenhouse warming, (E) although models predict greenhouse warming, there is no evidence in recent years that it may have in fact begun.

    Answer: The correct choice is (B) because methane is much more effective per molecule in the atmosphere in absorbing infrared radiation.

12. Of the following, the true statement pertaining to the "Antarctic ozone hole" is (explain): (A) It reaches its peak during the Antarctic summer, (B) it does not involve chlorine species, (C) it involves only species that occur in the gas phase, (D) it does not involve ClO radical, (E) it is related to species that are frozen in stratospheric cloud particles at very low temperature.

    Answer: (E)

13. Of the following, the one that is **not** an effect of acid rain is (explain): (A) Direct phytotoxicity (plant toxicity) from H^+, (B) phytotoxicity from acid-forming acid-forming gases, such as SO_2, (C) phytotoxicity from liberated Al^{3+}, (D) toxicity to fish fingerlings from acid accumulated in lakes, (E) all the above are effects.

    Answer: (E)

14. Of the following, the one that is **not** a measure for decreasing adverse effects on global climate is (explain): (A) Minimization, such as reducing emissions of greenhouse gases, (B) counteracting measures, such as injection of light-reflecting particles into the upper atmosphere, (C) replacement of nuclear energy with fossil energy, (D) adaptation, such as more efficient irrigation, (E) "tie-in" strategy

    Answer: (C)

15. Of the following, the true statement pertaining to "the Endangered Global Atmosphere" is (explain): (A) Atmospheric SO_2 may indirectly help reduce the greenhouse effect, (B)

atmospheric carbon dioxide levels are projected to decrease after the year 2010, (C) "nuclear winter" is of concern primarily for the greenhouse effect, (D) the major effect of volcanic eruptions is greenhouse warming, (E) photochemical smog is primarily a global problem, not regional or local.

Answer: (A)

16. Using the internet, look up the most recent near collision of a large, potentially very destructive, asteroid with Earth. When did it happen? How close did the asteroid come to Earth? How large was it? What would have been the likely effects of a collision?

Answer: As an example, on Nov. 1, 2016, the near-Earth asteroid 2016 VA was discovered just 1 day before it came within about 80,000 km (0.2 lunar distances) of Earth. At about 15 meters in diameter, it was too small to threaten massive damage to the planet, but a direct hit certainly would have caused a considerable blast, damage to structures such as blown out windows, and consternation.

Chapter 14
The Geosphere and Geochemistry

1. Of the following, the one that is **not** a manifestation of desertification is (explain): (A) Declining groundwater tables, (B) salinization of topsoil and water, (C) production of deposits of MnO_2 and $Fe_2O_3 \bullet H_2O$ from anoxic processes, (D) reduction of surface waters, (E) unnaturally high soil erosion.

   Answer: (C) would not be a manifestation of desertification because it requires an anoxic, wet reducing atmosphere to produce soluble Fe^{2+} and Mn^{2+} ions that are precursors to the production of deposits of MnO_2 and $Fe_2O_3 \bullet H_2O$ when the dissolved ions are exposed to the atmosphere, conditions unlike those in which deserts are formed.

2. Give an example of how each of the following chemical or biochemical phenomena in soils operates to reduce the harmful nature of pollutants (explain): (A) Oxidation-reduction processes, (B) hydrolysis, (C) acid-base reactions, (D) precipitation, (E) sorption, (F) biochemical degradation.

   Answer: (A) oxidation-reduction processes mediated by microorganisms detoxify and destroy many pollutants; (B) hydrolysis processes often mediated by microorganisms detoxify and destroy many pollutants; (C) acid-base reactions neutralize excessively acidic or basic pollutants; (D) precipitation reactions transform some pollutants, especially heavy metal ions, to less mobile and less toxic solid forms; (E) sorption onto minerals and soil removes pollutants from groundwater; (F) biochemical degradation processes mediated by microorganisms detoxify and destroy many pollutants.

3. Why do silicates and oxides predominate among earth's minerals?

   Answer: Because silicon and oxygen are the most abundant elements in Earth's crust

4. Give the characteristic that the minerals with the following formulas have in common: NaCl, Na_2SO_4, $CaSO_4 \bullet 2H_2O$, $MgCl_2 \bullet 6H_2O$, $MgSO_4 \bullet 7H_2O$, $KMgClSO_4 \bullet 1/4H_2O$, $K_2MgCa_2(SO_4)_4 \bullet 2H_2O$.

   Answer: These are all evaporates produced when water evaporates from brine.

5. Explain how the following are related: weathering, igneous rock, sedimentary rock, soil.

   Answer: Weathering converts igneous rock to soluble and finely divided forms that compose sedimentary rock; the final product of rock weathering is soil.

6. Match the following:

   (A) Metamorphic rock
   (B) Chemical sedimentary rocks
   (C) Detrital rock
   (D) Organic sedimentary rocks

   (1) Produced by the precipitation or coagulation of dissolved or colloidal weathering products
   (2) Contain residues of plant and animal remains
   (3) Formed from action of heat and pressure on sedimentary rock
   (4) Formed from solid particles eroded from igneous rocks as a consequence of weathering

   Answer: (A)-(3), (B)-(1), (C)-(4), (D)-(2)

7. Where does most flowing water that contains dissolved load originate? Why does it tend to come from this source?

   Answer: Dissolved load in water originates with groundwater, which is in the most intimate contact with minerals that produce dissolved load.

8. What role might be played by water pollutants in the production of dissolved load and in the precipitation of secondary minerals from it?

   Answer: Acidic water pollutants tend to dissolve minerals such as $CaCO_3$. In the presence of pollutant base, $CaCO_3$ may precipitate.

9. As defined in this chapter, are the ions involved in ion replacement the same as exchangeable cations? If not, why not?

   Answer: The ions involved in ion replacement are those that substitute for mineral constituents of a higher oxidation state, such as Al(III) substituting for Si(IV) within the mineral matrix. These ions are not readily exchangeable with other ions.

10. Speculate regarding how water present in poorly consolidated soil might add to the harm caused by earthquakes.

    Answer: Water in poorly consolidated soil tends to make such soil behave like a liquid in earthquakes such that it behaves like "a bowl full of jelly" thus magnifying the effects of the quake.

11. In what sense may volcanoes contribute to air pollution? What possible effects may this have on climate?

    Answer: Volcanoes mainly add sulfur dioxide to the atmosphere, either directly or as H_2S that is oxidized to sulfur dioxide. This sulfur is eventually converted to sulfuric acid aerosol droplets that reflect sunlight and cause a cooling effect. Severe volcanic eruptions may put enough fine particulate matter into the atmosphere to also have a cooling effect.

12. Explain how excessive pumping of groundwater might adversely affect streams, particularly in regard to the flow of small streams.

    Answer: Excessive pumping of groundwater can lower water tables causing streams fed by groundwater to dry up.

13. Which three elements are most likely to undergo oxidation as part of chemical weathering process? Give example reactions of each.

    Answer: Iron, manganese, and sulfur are the major elements that undergo oxidation as part of the weathering process. The following reaction shows oxidation of both iron and sulfur during weathering:

    $4FeS_2(s) + 15O_2(g) + (8 + 2x)H_2O \rightarrow 2Fe_2O_3 \cdot xH_2O(s) + 8SO_4^{2-}(aq) + 16H^+(aq)$

    Manganese is probably oxidized from Mn(II) in a mineral such as $MnCO_3$ to Mn(IV):

    $2MnCO_3(s) + O_2(g) \rightarrow 2MnO_2(s) + 2CO_2(g)$

14. Match the following:

    (A) Groundwater — (1) Water from precipitation in the form of rain or snow
    (B) Vadose water — (2) Water present in a zone of saturation
    (C) Meteoric water — (3) Water held in the unsaturated zone or zone of aeration
    (D) Water in capillary — (4) Water drawn somewhat above the water table by surface tension

    Answer: (A)-(2), (B)-(3), (C)-(1), (D)-(4)

15. Large areas of central Kansas have vast deposits of halite. What is halite? What does this observation say about the geologic history of the area?

Answer: Halite is NaCl. Its presence shows that the area was once covered by a sea from which the water evaporated leaving solid NaCl behind.

16. What is the distinction between weathering and erosion? Suggest ways in which air pollution may contribute to both phenomena.

Answer: Weathering is the physical and chemical breakdown of rock whereas erosion is the physical movement of rock or soil by the action of wind or flowing water. Air pollution by acid-forming gases may increase weathering by action of H^+ ion. Pollution by greenhouse gases can lead to drought conditions conducive to wind erosion.

17. One way in which coal and other fossil fuels may be used without contributing to higher levels of greenhouse gas carbon dioxide in the atmosphere is through carbon sequestration by pumping carbon dioxide into mineral strata. Explain with a chemical reaction how formations of limestone (calcium carbonate) might be used for this purpose. Suggest how this might cause problems on the surface.

Answer: Calcium carbonate undergoes the following reaction with CO_2:

$CaCO_3(s) + CO_2(g) + H_2O(l) \rightarrow Ca^{2+}(aq) + 2HCO_3^-(aq)$

This reaction puts gaseous CO_2 into solution as HCO_3^- ion. By dissolving the $CaCO_3$ rock, however, it leaves voids in the rock formation that can lead to subsidence.

18. Deposits of iron minerals are often found where groundwater flows to the surface. Use a chemical reaction to explain this observation.

Answer: Soluble Fe^{2+} ion dissolved in water becomes oxidized to deposits of iron(III) oxide when exposed to atmospheric O_2: $4Fe^{2+}(aq) + O_2(g) + 4H_2O(l) \rightarrow 2Fe_2O_3(s) + 8H^+$

Chapter 15
Soil: Earth's Lifeline

1. Give two examples of reactions involving manganese and iron compounds that may occur in waterlogged soil.

   Answer: $MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$
   $Fe_2O_3 + 6H^+ + 2e^- \rightarrow 2Fe^{2+} + 3H_2O$

2. What temperature and moisture conditions favor the buildup of organic matter in soil?

   Answer: Lower temperatures and higher moisture

3. "Cat clays" are soils containing a high level of iron pyrite, FeS_2. Hydrogen peroxide, H_2O_2, is added to such a soil, producing sulfate as a test for cat clays. Suggest the chemical reaction involved in this test.

   Answer: $FeS_2 + {}^{15}/_2H_2O_2 \rightarrow Fe^{3+} + H^+ + 2SO_4^{2-} + 7H_2O$

4. What effect upon soil acidity would result from heavy fertilization with ammonium nitrate accompanied by exposure of the soil to air and the action of oxic bacteria?

   Answer: Oxidation of the N in NH_4^+ to nitrate would produce nitric acid and make the soil more acidic

5. How many moles of H^+ ion are consumed when 200 kilograms of $NaNO_3$ undergo denitrification in soil?

   Answer: If the denitrification reaction is represented as the following, where $\{CH_2O\}$ is biodegradable organic matter,

   $4NO_3^- + 5\{CH_2O\} + 4H^+ \rightarrow 2N_2 + 5CO_2 + 7H_2O$

   the mol ratio of H^+ to NO_3^- is 1/1. The molar mass of $NaNO_3$ is 85.0 kg/kmol so in 200 kg of $NaNO_3$ there are 200 kg/85.0 kg/kmol = 2.35 kmol or 2,350 mol of H^+ ion.

6. What is the primary mechanism by which organic material in soil exchanges cations?

   Answer: The major organic constituent of soil is humus (humic material). Humic substances contain the carboxylate, $-CO_2^-$, group, which binds with and exchanges cations.

7. Prolonged waterlogging of soil does **not** (A) increase NO_3^- production, (B) increase Mn^{2+} concentration, (C) increase Fe^{2+} concentration, (D) have harmful effects upon most plants, (E) increase production of NH_4^+ from NO_3^-.

   Answer: The correct answer is (A) because waterlogging causes reducing conditions whereas NO_3^- is an oxidized form of nitrogen.

8. Of the following phenomena, the one that eventually makes soil more basic is (A) removal of metal cations by roots, (B) leaching of soil with CO_2-saturated water, (C) oxidation of soil pyrite, (D) fertilization with $(NH_4)_2SO_4$, (E) fertilization with KNO_3.

   Answer: The correct answer is (E) because conversion of the nitrogen in KNO_3 to N_2 leaves a basic residue.

9. How many metric tons of farm manure are equivalent to 100 kg of 10-5-10 fertilizer?

Answer: Farm manure is equivalent to a 0.5-0.24-0.5 fertilizer which is only 1/20 as strong as a commercial 10-5-10 fertilizer so 20 times as much manure would be required. This would be 2000 kg or 2.0 metric tons.

10. How are the chelating agents that are produced from soil microorganisms involved in soil formation?

Answer: They tend to dissolve metals in minerals leading to the breakdown of rock as part of the weathering process

11. What specific compound is both an animal waste product and a major synthetic fertilizer?

Answer: Urea

12. What happens to the nitrogen/carbon ratio as organic matter degrades in soil?

Answer: During the humification process the nitrogen/carbon ratio of the organic matter increases as carbon is lost to CO_2 evolved during biodegradation and nitrogen fixed by nitrogen-fixing bacteria is incorporated into the humic residue.

13. To prepare a rich potting soil, a greenhouse operator mixed 75% "normal" soil with 25% peat. Estimate the cation-exchange capacity in milliequivalents/100 g of the product.

Answer: The cation-exchange capacity of peat may range from 300-400 meq/100 g. Values of cation-exchange capacity for soils with more typical levels of organic matter are around 10-30 meq/100 g. For the potting soil given, an estimate of the cation-exchange capacity, taking the averages of the cation-exchange capacities given above, could be the following:

$$\text{CEC} = 75\text{ g} \times 0.2\text{ meq/g} + 25\text{ g} \times 3.5\text{ meq/g} = 102.5\text{ meq/100 g}$$

14. Explain why plants grown on either excessively acidic or excessively basic soils may suffer from calcium deficiency.

Answer: In excessively acidic soils, H^+ competes with Ca^{2+} for uptake by roots and acid-soluble $CaCO_3$ dissolves and the calcium is leached from the soil. In excessively basic soils the solubility of Ca^{2+}, especially in respect to $CaCO_3$, is lowered so that the Ca^{2+} is not readily available to the plants. Basic soils also have relatively high concentrations of Na^+ in the soil solution, which competes with Ca^{2+} for uptake by roots.

15. What are two mechanisms by which anions may be held by soil mineral matter?

Answer: At low pH, a metal oxide surface may have a net positive charge enabling it to hold anions, such as chloride, by electrostatic attraction. At higher pH values, the soil mineral surface may have a net negative charge due to the formation of OH^- ion on the surface caused by loss of H^+ from the water molecules bound to the surface. In such cases, it is possible for anions such as HPO_4^{2-} to displace hydroxide ion and bond directly to the oxide surface.

16. What are the three major ways in which pesticides are degraded in or on soil?

Answer: The most important is biodegradation. Chemical degradation and breakdown by photochemical reactions may also occur.

17. Lime from lead mine tailings containing 0.5% lead was applied at a rate of 10 metric tons per acre of soil and worked in to a depth of 20 cm. The soil density was 2.0 g/cm^3. To what extent did this add to the burden of lead in the soil? There are 640 acres per square mile and 1,609 meters per mile.

$$\frac{10 \times 10^6\text{ g tailings} \times 0.005\text{ g lead/g tailings}}{1.62 \times 10^9\text{ g soil}} = 0.000031 = 31\text{ parts per million (ppm)}$$

18. Match the soil or soil-solution constituent in the left column with the soil condition described on the right, below:

(1) High Mn^{2+} content in soil	(A) "Cat clays" containing initially high levels of pyrite, FeS_2
(2) Excess H^+	
(3) High H^+ and SO_4^{2-} concentrations	(B) Soil in which biodegradation has not occurred to a great extent
(4) High organic content	(C) Waterlogged soil
	(D) Soil, the fertility of which can be improved by adding limestone.

Answer: (1)-(C), (2)-(D or A), (3)-(A), (4)-(B or in come cases C)

19. What are the processes occurring in soil that operate to reduce the harmful effects of pollutants?

Answer: Sorption, biodegradation, ability to neutralize acidic or basic pollutants (soil acting as a buffer).

20. Under what conditions do the reactions below occur in soil? Name two detrimental effects that can result from these reactions.

$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$ and

$Fe_2O_3 + 6H^+ + 2e^- \rightarrow 2Fe^{2+} + 3H_2O$

Answer: These processes tend to occur in waterlogged anoxic soils. The metal cations can be toxic to plants and reprecipitation of MnO_2 and Fe_2O_3 can clog drainage tiles in soil.

21. What are four important effects of organic matter in soil?

Answer: (1) it serves as a food source for microorganisms; (2) undergoes important chemical reactions such as ion exchange; (3) influences the physical properties of soil; and (4) contributes to the formation of soil by influencing the weathering of mineral matter.

22. How might irrigation water treated with fertilizer containing potassium and ammonia become depleted of these nutrients in passing through humus-rich soil?

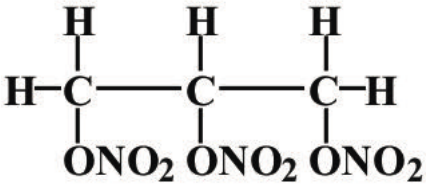
Answer: Both K^+ and NH_4^+ can be removed from the water and bound to soil humus by cation-exchange processes.

Chapter 16
The Anthrosphere: Industrial Ecology and Green Chemistry

1. Although abundant, why is lignin not a good candidate as a raw material?

   Answer: Lignin's highly variable nature and refractory character with respect to chemical and biochemical processes makes it relatively unsuitable as a raw material.

2. What structural features of the compound shown below would make it hazardous? What is the nature of the hazard?



   Answer: The abundance of functional groups in which oxygen atoms are bound to nitrogen atoms on a hydrocarbon skeleton means that it has both oxidizing and reducing capabilities in the same compound. It is reactive and explosive.

3. What is the potential use of dialkyl carbonates, such as dimethyl carbonate, in green chemical synthesis?

   Answer: These carbonates are alkylating agents that act to attach alkyl (methyl) groups to other molecules without leaving hazardous residues. The processes for making the compounds are relatively green.

4. What are some uses of organic solvents other than for reaction media? What are some of the drawbacks of organic solvents for these uses?

   Answer: In addition to serving as media for organic reactions, organic solvents are used to carry organic-soluble reagents to a reaction medium, as vehicles in paints and coatings, and for cleaning parts. Major disadvantages of organic solvents in these applications are their tendencies to evaporate and pollute air and their toxic nature. The purification of spent solvents and the destruction and disposal of residues left from the distillation of spent solvents may also present challenges.

5. In terms of interaction with reagents, what is the greatest disadvantage of water as a solvent? What is the greatest advantage of water as a solvent for a variety of solutes of biological origin?

   Answer: Water is a poor solvent for many organic reagents and may react with some reagents, largely by hydrolysis reactions. A big advantage of water for solutes of biological origin is that these materials are largely created in a water medium by biochemical reactions and are compatible with water.

6. What is a dense phase fluid? What form of dense phase carbon dioxide is produced at very high pressures and slightly elevated temperature?

   Answer: A dense phase fluid is a highly compressed, somewhat dense substance that may be a supercritical fluid, highly compressed gas, or mixture of gas and liquid.

7. What are the advantages of supercritical fluid carbon dioxide solvent? Why is carbon dioxide's volatility an advantage in some cases?

   Answer: Supercritical carbon dioxide is widely available, a good solvent for organic solutes, readily removed by evaporation, and non-polluting, except as a greenhouse gas if allowed to escape.

8. Discuss how electrons and photons can be regarded as catalysts. In what respects are they "massless" reagents?

   Answer: In a sense, both electrons and photons are catalytic in that they enable or cause reactions to occur. Unlike true catalysts, they are "used up" in a chemical reaction. Adding electrons (reduction), removing electrons (oxidation), and subjecting reagents to photons does not change the mass of material involved in a chemical reaction, so these materials can be regarded as "massless" reagents.

9. Look up on the internet the Haber process for the synthesis of ammonia. Discuss and compare the conditions and relative advantages and disadvantages of the Haber process and its biological alternatives within the context of green chemistry.

   Answer: As discussed in Chapter 15, Section 15.7, ammonia is made by the Haber process, in which N_2 and H_2 are combined over a catalyst at temperatures of approximately 500°C and pressures up to 1000 atm:

   $$N_2 + 3H_2 \rightarrow 2NH_3$$

   The chemical synthesis of ammonia is a green process in that the nitrogen is taken from air and the hydrogen can be made by the electrolysis of water, although in practice it is usually made by steam reforming of natural gas, CH_4. However, this synthesis requires significant amounts of energy and generally severe conditions that are not in keeping with the best practice of green chemistry. The biological alternative is one in which bacteria fix atmospheric nitrogen into biomolecules (see the discussion of *Rhizobium* bacteria in Chapter 15). All the required ingredients come from air and water, the conditions are mild because of the benign conditions that the nitrogen-fixing bacteria require for their existence and metabolism, and the process is ultimately solar-powered through the utilization of photosynthetically-produced biomass.

10. Look up the Presidential Green Chemistry Award on the internet. From the information obtained, list several examples of green chemistry that have been put into practice on an industrial scale.

    Answer: Good sources of information on this topic include issues of *Chemical and Engineering News* published by the American Chemical Society and the website of the American Chemical Society's Green Chemistry Institute. Examples of the application of green chemistry are given in these references.

11. What is the relationship of industrial ecology to green chemistry? In which ways are industrial ecology and green chemistry complementary?

    Answer: Green chemistry can be regarded largely as the chemical component of the best practice of industrial ecology. Each is an integral part of the other.

12. What is the meaning of "command and control?" What are its limitations in the control of pollution?

    Answer: "Command and control" mandates limits to pollution through laws and regulations. It is limited by several factors including costs and the need for careful monitoring to ensure that limits are not exceeded.

13. In what sense does the practice of green chemistry ensure environmental quality by "natural," self-regulating means?

    Answer: Examination of the "Twelve Principles of Green Chemistry" in Section 16.2 shows that for the most part adherence to these guidelines ensures good environmental quality and limits pollution. By its emphasis on safe reagents and products, green chemistry prevents release of harmful pollutants to the environment. The high efficiency of material utilization in the practice of green chemistry means that there is less potentially polluting waste released to the environment.

14. What is the role of sustainability in the practice of green chemistry?

    Answer: By its nature, green chemistry is sustainable chemistry.

15. How is atom economy defined? In what sense is it a key aspect of the practice of green chemistry?

    Answer: Atom economy is the fraction of reactant material that actually ends up in final product. Achievement of a high degree of atom economy ensures most efficient utilization of reagents and minimum production of waste making it a key aspect of the practice of green chemistry.

16. Look up the phenomenon of mineralization as it occurs in biological ecosystems. Name and describe a process analogous to mineralization that occurs in an industrial ecosystem.

    Answer: Mineralization refers to biodegradation processes in which often complex organic materials are broken down to simple inorganic substances such as carbon dioxide from organic carbon, ammonium ion from organic nitrogen, and phosphate from organophosphorous compounds. Analogies in an industrial ecosystem would be production of iron from steel in car bodies or aluminum metal from aluminum beverage cans.

17. How are the terms industrial metabolism, industrial ecosystem, and sustainable development related to industrial ecology?

    Answer: Industrial ecology is practiced in industrial ecosystems where materials undergo industrial metabolism. Sustainable development refers to utilization of materials, energy, and resources in a way that minimizes their depletion such as by using renewable materials (for example, biomass feedstocks), renewable energy (for example, wind energy), and recycling of materials.

18. From the definition of symbiosis, explain what is meant by industrial symbiosis. How is industrial symbiosis related to industrial ecology?

    Answer: In nature, symbiosis refers to two or more organisms that function to mutual advantage, such as the algae and fungi present in lichens that grow on rocks. Substitution of industrial enterprises for organisms in this definition defines industrial symbiosis, which is an integral part of the practice of industrial ecology.

19. Justify or refute the statement that in an operational industrial ecosystem only energy is consumed.

    Answer: In an ideal industrial ecosystem, all materials are conserved. Energy is not really consumed, but in being utilized for production is converted ultimately to a form that has no further uses and in that sense is "consumed."

20. In what sense is the consumer sector the most difficult part of an industrial ecosystem?

    Answer: Materials and items that get into the consumer sector tend to become dispersed, which makes their collection for reuse and recycling relatively difficult.

21. In what sense might a "moon station" or a colony on Mars advance the practice of industrial ecology?

    Answer: The cost of transporting materials from Earth to the moon or Mars would be extremely high thereby mandating efficient material utilization.

22. Look up some information regarding the nature of electronic apparatus in the 1940s and 1950s. In what sense do modern solid-state electronic devices illustrate both dematerialization (use of less material) and material substitution (substitution of more readily available materials for those that are scarce)?

    Answer: Radios, television sets, and early computers used bulky, energy-consuming vacuum tubes, circuits composed of insulated wires soldered together, and other material- and energy-consuming components. The introduction of the transistor and integrated circuits printed on circuit boards reduced the need for materials required for electronic apparatus by orders of magnitude. It may not be too much of an exaggeration to assert that using electronic components of 1940s vintage to construct a computer with the capabilities of a modern laptop would fill a university fieldhouse and require a substantial dedicated powerplant to run it (plus armies of technicians on duty at all times to test and replace failing vacuum tubes). An excellent example of material substitution is the use of abundant (though highly purified) silica in place of scarce and expensive copper for communications transmission.

23. What are the enterprises that serve to underpin the Kalundborg industrial ecosystem? How might they compare with the basic enterprises of an industrial ecosystem consisting of rural counties in the state of Iowa?

    Answer: The two main enterprises in the Kalundborg industrial ecosystem are a large coal-fired electrical plant and a large petroleum refinery. An industrial ecosystem in a rural area could consist of agricultural land devoted to growing biomass, livestock feeding operations using the biomass food source, methane-producing anoxic digesters to produce high-quality fuel from livestock wastes, and biorefineries to refine chemical products from thermally treated biomass.

24. How does "design for recycling" (DFR) relate to embedded utility?

    Answer: As shown in Figure 16.11 illustrating an "energy/materials pyramid," significantly less energy, and certainly no more materials, are involved when recycling is performed near the top of the materials flow chain rather than near the bottom. The more efficient recycling near the top of the pyramid can be facilitated when components are designed to best enable recycling such as by easy separation of components in intact form from the apparatus of which they are a part.

25. Distinguish among consumable, durable (service), and recyclable products.

    Answer: Consumable products, such as natural gas furnace fuel, are "used up" and their products dissipated to the environment (carbon dioxide and water vapor exhausted to the atmosphere in the combustion of natural gas). A durable product would be the toner cartridge in a laser printer, which can be refilled with toner, refurbished, and returned to the market (the toner itself being a consumable product). Refrigerant fluids are examples of recyclable commodities that can be reused (if not lost to the atmosphere through leakage).

26. List some of the "environmentally friendly" criteria met by soap as a consumable commodity.

    Answer: Soap is environmentally friendly as a product because it is biodegradable and precipitates from water in the presence of calcium ion (the solid calcium precipitates can be

unsightly, but eventually biodegrade). Soap is made from renewable materials including waste animal fats and vegetable oils. The sodium hydroxide used to react with fats and oils to make soap is made by electrolysis of a solution of sodium chloride, of which there are inexhaustible resources in underground salt deposits and saline groundwater brines. Assuming a use for the chlorine and hypochlorite byproduct of this electrolytic synthesis it can be regarded as 100% atom efficient. However, chlorine is toxic and can present disposal problems.

27. Consider a university as an industrial ecosystem in which the ultimate "consumer" is society that utilizes and benefits from educated graduates. Describe ways in which the university fits the model of an industrial ecosystem and ways in which it does not. Is there any recycling? Can you suggest ways in which a university might become a more efficient ecosystem?

    Answer: The answer to this question can be very long and detailed, limited mainly by the imagination and knowledge of universities possessed by the person answering it. The raw material in the form of student bodies is a renewable resource. The production of PhDs who come back to teach in a university can be considered a form of recycling as can knowledge obtained in university research that is incorporated back into the curriculum. The return of former students who need updated skill sets can be considered a form of recycling. If one considers imparting of factual knowledge and skills to students aside from the issue of teaching them "critical thinking," an argument can be made that universities are models of inefficiency that are far too costly in areas such as tuition costs and expenses for textbooks. Much more effective utilization of computerized instruction and testing along with internet resources are making parts of some universities much more efficient.

28. Suppose that it is proposed to construct a huge system to divert a significant amount of water from near the mouth of the Mississippi River and pump it with power provided by giant wind farms in Texas across the southern U.S. and into southern California and northern Mexico. Suggest how such a project might constitute an industrial ecosystem and what it would include. Suggest advantages and possible disadvantages.

    Answer: The potential of such a system to meet needs for water, energy, and agricultural products is significant. With a reliable source of affordable water, large areas of agricultural land could be developed. Industries that require water and wind-generated energy could develop throughout the length of the system. Diversion of large amounts of fresh water from "nature's path" to the sea could be a disadvantage, although, as discussed in the answer to the next question, could actually offer some significant benefits.

29. The Mississippi River water that would be used in the project suggested in the preceding question contains algal (plant) nutrients in the form of phosphates, inorganic nitrogen, and potassium that cause excessive plant growth (eutrophication) in large regions of the Gulf of Mexico near the mouth of the river. The water also contains relatively high levels of oxygen-demanding organics, silt, and some industrial chemicals which, along with eutrophication, result in the formation of a "dead zone" at certain times of the year in the Gulf of Mexico. Suggest how ecological engineering could be applied to the proposed water project to mitigate these water pollution problems and deliver a clean water product to the end users.

    Answer: Water could be diverted to containment structures near the point of discharge and retained for a period of time during which solid materials could settle eventually leading to build-up areas of "constructed" land. Fertilized by contaminant fertilizer runoff in the river water, it is likely that aquatic plant life would thrive in these areas removing nutrients that otherwise would contribute to eutrophication and formation of the "dead zone" in the Gulf of Mexico. To an extent, such an ecological engineering project could reduce coastal erosion.

30. Globalization of economies is a contentious issue. Suggest how globalization may relate to the practice of industrial ecology. Suggest ways in which globalization may help and may hurt the proper practice of industrial ecology.

    Answer: Globalization contributes to diversity in industrial production, which is in keeping with the best practice of industrial ecology. By its close physical proximity to material resources and/or readily available human resources, globalization aids efficient production. A disadvantage is that globalization may scatter enterprises over thousands of kilometers distance making it much harder for various enterprises to connect physically in industrial ecosystems.

Chapter 17
Resources and Sustainable Materials

1. Lead, zinc, and copper, are often associated with hydrothermal deposits and commonly occur as the metal sulfides. What does this suggest about the pE conditions (see Chapter 3) in the hydrothermal waters under which these deposits were formed?

   Answer: Sulfides (H_2S, HS^-, and S^{2-}) that produce solid metal sulfides (PbS, ZnS, CuS) are formed under low pE conditions.

2. The world's largest trona deposit is in the Green River Basin of Wyoming. Look up trona on the internet and suggest how this deposit was formed.

   Answer: Trona is an evaporite mineral, a hydrated double salt of sodium carbonate and sodium bicarbonate, formula $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$. The largest known deposit is the Green River formation in Wyoming which remained from the evaporation of a huge lake during the Paleogene period that began 65 million years ago and ended 23 million years ago.

3. It is believed that Earth's oceans before the emergence of living organisms in them contained large amounts of dissolved Fe^{2+}. Describe with chemical reactions how this iron was converted to deposits of Fe_2O_3, an important iron ore, by biochemical and chemical processes. Consider the solubility of $Fe(OH)_3$ and what happens to it when it is heated.

   Answer: As elemental oxygen was evolved by photosynthesis of early cyanobacteria through the process represented as $CO_2 + H_2O + h\nu \rightarrow \{CH_2O\} + O_2$, the following reaction took place between the O_2 product and dissolved Fe^{2+}:

   $4Fe^{2+}(aq) + O_2 + 10H_2O \rightarrow 4Fe(OH)_3(s) + 8H^+$

   The initially highly hydrated $Fe(OH)_3(s)$ in ocean sediments became buried and subjected to high temperatures leading to the following reaction and Fe_2O_3 product:

   $4Fe(OH)_3 \rightarrow 2Fe_2O_3 + 6H_2O$

4. Using internet resources, look up the chemical reactions involved in extraction of gold from ore with cyanide. Why are the solutions maintained at a relatively high pH? What are the environmental implications of the process?

   Answer: Gold is extracted from its ore with a solution of sodium cyanide, which extracts the gold as a soluble gold cyanide. The high pH is required to keep the cyanide in the reactive form of cyanide ion, CN^-. At lower pH values toxic hydrogen cyanide vapor would form. Incidents have occurred in which release of cyanide solution from gold leaching operations has contaminated streams leading to fish kills.

5. Calculate approximately how many tons of tailings were produced per ton of copper metal recovered from ore in 1900 compared to now. What are the environmental implications of these figures.

   Answer: Examination of Figure 17.1 indicates that in 1900 the average copper ore was about 4% copper whereas now it is around 0.5% copper. In 1900 to recover a ton of copper metal from ore required about 1 ton/0.04 = 25 tons of ore of which almost 24 tons ended up as tailings. (The first step in refining copper sulfide ore is "roasting" in which the sulfur in CuS is converted to SO_2, which was discharged to the atmosphere during early days of copper

metallurgy.) Currently the amount of ore that must be processed to produce one ton of copper = 1 ton/0.005 = 200 tons, essentially all of which consists of tailings.

6. Although very rare in nature, why was gold one of the first metals discovered and used by humans? From what you can learn about the chemistry of copper and that of iron, suggest why copper metal was discovered and used before iron. Although iron almost never occurs in the elemental form in that part of Earth's crust accessible to humans, suggest how elemental iron was discovered. Where might elemental iron have been observed in nature in very rare and spotty locations around Earth?

   Answer: Gold occurs in the elemental form which, although extremely rare, was easy for humans to melt and form. Copper occurs mostly in a chemically combined form, although deposits of metallic copper do exist, and these were probably first discovered and used by humans. Iron metal may well have been observed where iron-rich minerals were exposed to reducing conditions in a charcoal fire leading to the idea of heating the minerals mixed with burning charcoal to recover iron. Pure iron is found in some meteorites discovered in widely scattered locations over Earth's surface.

7. What is the chemical reaction for the calcination of the aluminum compound precipitated from bauxite? In what two respects is the production of aluminum from ore energy-intensive? How does aluminum metal recycling reduce the consumption of energy in aluminum production?

   Answer: Aluminum hydroxide extracted from bauxite ore is precipitated in the pure form at lower temperatures and calcined at about 1200°C to produce pure anhydrous Al_2O_3. The heat for the calcination process requires energy. The anhydrous alumina is electrolyzed in molten cyrolite, Na_2AlF_6, at carbon electrodes to produce aluminum metal, a process that consumes large amounts of electricity. Recycling of aluminum metal simply requires melting it with heat and casting into some form suitable for processing, which requires much less energy than refining the metal from the ore.

8. What were two applications of lead that lead to its widespread dispersal in the environment until about the 1970s?

   Answer: Lead in the form of organometallic tetraethyllead was added as an octane booster to gasoline and dispersed throughout the environment with automotive exhausts. It was also an ingredient in lead-pigmented paints and metal primer formulations. Lead in plumbing has also added to environmental contamination by lead.

9. What environmental measures have the potential to lead to a surplus of sulfur?

   Answer: Reclamation of sulfur from sulfur-containing coal, natural gas containing H_2S, and petroleum could lead to a surplus of the sulfur commodity.

10. What are the chemical processes for extracting cellulose from wood to make paper? Why are these environmentally problematic? Look up the chemical composition of cotton and suggest why it can be used to make an especially good (but expensive) grade of paper.

    Answer: Sulfite and strong base are both used to isolate the useless lignin fraction of wood from the cellulose required to make paper. Cotton is essentially pure cellulose from which it is simpler to make high-grade paper than is using wood as a feedstock.

11. Two of the main approaches that employ the practice of industrial ecology for using smaller amounts of material and more readily available substances are dematerialization and material substitution. Compare the nature of electronics and communications apparatus from the 1950s to the corresponding apparatus used today and show how both dematerialization and

material substitution have lead to much less use of materials in electronics and communications.

Answer: Radios, television sets, and early computers used bulky, energy-consuming vacuum tubes, circuits composed of insulated wires soldered together, and other material- and energy-consuming components. The introduction of the transistor and integrated circuits printed on circuit boards reduced the need for materials required for electronic apparatus by orders of magnitude. It may not be too much of an exaggeration to assert that using electronic components of 1940s vintage to construct a computer with the capabilities of a modern laptop would fill a university fieldhouse and require a substantial dedicated powerplant to run it (plus armies of technicians on duty at all times to test and replace failing vacuum tubes). An excellent example of material substitution is the use of abundant (though highly purified) silica in place of scarce and expensive copper for communications transmission.

12. According to information from the U.S. National Renewable Energy Laboratory, "industrial biorefineries have been identified as the most promising route to the creation of a new domestic biobased industry." What is a biorefinery? How does it compare to a petroleum refinery? How can the widespread application of biorefineries aid sustainability?

    Answer: A petroleum refinery is used to separate the hydrocarbons in petroleum into various fractions and chemically modify the separated materials to obtain desired products, such as high-octane gasoline. Similarly, a biorefinery is used to isolate the various materials from biomass feedstocks. These differ from petroleum ingredients in that biomass consists largely of organo-oxygen compounds (often represented as $\{CH_2O\}$ and, in some cases, oils that contain only small amounts of oxygen and have empirical formulas similar to those of hydrocarbons and even pure hydrocarbons, such as in terpenes. Part of the biorefinery process can be chemical modification of the separated materials to give desired products. An example is hydrolysis of oils to yield long-chain fatty acids followed by synthesis of methyl esters to give biodiesel fuel. Widespread deployment of biorefineries can contribute greatly to sustainability by facilitating the use of renewable biomass feedstocks in place of depleting petroleum.

13. Although alloys greatly increase the utility of metals, how does alloying potentially make the recycling of metals more difficult?

    Answer: Alloys are mixtures of different metals. Since an alloy is basically a solution in which metals are mixed at the atomic level, it is not practical to separate the metals, which complicates recycling.

14. What are two reasons that plastics are generally less recyclable than metals? Why are thermosetting plastics less recyclable than thermoplastics?

    Answer: Plastics have much less inherent monetary value than metals and in many cases cannot be melted and recast as can metals. Thermosetting plastics are those that set up at elevated temperatures and cannot be melted for recycling.

15. Why are present practices for recycling lubricating oils much more sustainable than those employed in decades past?

    Answer: Present practices rely largely upon distillation to separate motor oil constituents for recycling. Formerly, treatment with clay and sulfuric acid were used, which left large quantities of residues requiring disposal.

Chapter 18
Sustainable Energy: The Key to Everything

1. The tail of a firefly glows, although it is not hot. Explain the kind of energy transformation that is involved in the firefly's production of light.

   Answer: The process is chemiluminescence in which a chemical reaction produces photons of light.

2. What is the standard unit of energy? What unit did it replace? What is the relationship between these two units?

   Answer: The standard unit of energy is the joule, abbreviated J, which replaced the calorie (1 cal = 4.184 J)

3. Which law states that energy is neither created nor destroyed?

   Answer: The first law of thermodynamics states that energy is neither created nor destroyed.

4. What is the special significance of 1,340 watts with respect to potential energy sources?

   Answer: It is the solar flux equal to the power per square meter of sunlight at the distance of Earth from the sun.

5. What is the reaction in nature by which solar energy is converted to chemical energy?

   Answer: Photosynthesis in which energy in photons from the sun ($h\nu$) is fixed as chemical energy in biomass, represented as $\{CH_2O\}$:

   $CO_2 + H_2O + h\nu \rightarrow \{CH_2O\} + O_2$

6. In what respects is wind both one of the oldest, as well as one of the newest, sources of energy?

   Answer: Wind has been used for millennia to propel sailing ships and for centuries to power windmills. In the modern form as wind-powered generators, wind is the fastest growing form of renewable energy.

7. What are two major problems with reliance upon coal and petroleum for energy despite their relatively high abundance?

   Answer: Neither is a renewable energy source and both contribute greenhouse-warming carbon dioxide to the atmosphere.

8. Why does natural gas contribute less to greenhouse warming than does petroleum and much less than coal?

   Answer: The combustion of both carbon and bound hydrogen in fossil fuels provides energy, the former contributing greenhouse-warming carbon dioxide to the atmosphere and the latter water vapor. A higher proportion of water vapor in the atmosphere means a lower proportion of carbon dioxide per unit heat energy released. The empirical formula of methane in natural gas is CH_4, that of petroleum is approximately CH_2, and that of coal approximately CH. Per mole of carbon burned and of CO_2 produced, petroleum produces twice as much H_2O and methane 4 times as much H_2O as does coal.

9. How might coal be utilized for energy without producing greenhouse gas carbon?

Answer: By sequestering carbon dioxide produced in coal combustion or gasification and pumping it below ground.

10. What is a large limiting factor in growing biomass for fuel, and in what respect does this limit hold hope for the eventual use of biomass fuel?

    Answer: The very low efficiency with of photosynthesis is a large limiting factor in growing biomass for fuel. Genetically engineering plants for greater photosynthetic efficiency could substantially increase the yield of biomass fuel.

11. What relationship describes the limit to which heat energy can be converted to mechanical energy?

    Answer: The efficiency for the conversion of thermal to mechanical energy is given by the Carnot equation,

$$\text{Percent efficiency} = \frac{T_1 - T_2}{T_1} \times 100$$

    in which T_1 is the inlet temperature (for example, of steam into a steam turbine), and T_2, is the outlet temperature, both expressed in Kelvin (°C + 273).

12. Why does a diesel-powered vehicle have significantly better fuel economy than a gasoline-powered vehicle of similar size?

    Answer: Due to its high compression ratio, the diesel engine has a higher peak temperature (T_1 in the Carnot equation above) and is therefore relatively more efficient in converting the heat provided by fuel combustion to mechanical energy.

13. Why is a nuclear power plant less efficient in converting heat energy to electricity than is a fossil-fueled power plant?

    Answer: Because of limitations to the peak temperature that can be allowed in a nuclear reactor and in the fluids used to transmit heat from the reactor core, the value of T_1 in the Carnot equation for a nuclear reactor is lower than in a fossil-fueled powerplant.

14. Instead of having a spark plug that ignites the fuel, a diesel engine has a glow plug that operates only during engine startup. Explain the operation of the glow plug.

    Answer: After a diesel engine is started, the high temperature developed in the hot engine cylinders at the peak of compression when the fuel is injected causes ignition to occur spontaneously. During startup of a cold engine, the glow plugs provide the high temperature needed.

15. Cite two examples of vastly increased efficiency of energy utilization that took place during the 1900s.

    Answer: The replacement of steam locomotives with diesel locomotives and increased peak temperatures for steam turbines in power plants both increased energy efficiency. There are many other examples.

16. Describe a combined power cycle. How may it be tied with district heating?

    Answer: A combined power cycle including heating buildings with exhaust steam from steam turbines (district heating) is shown in Figure 18.28.

17. What are three reactions used in biomass gasification?

    $\{CH_2O\} + O_2 \rightarrow CO_2 + H_2O + \text{heat}$

    $\{CH_2O\} + {}^1/_2O_2 \rightarrow CO + H_2O + \text{heat}$

$\{CH_2O\} + \text{heat} \rightarrow C + H_2O$

$C + H_2O + \text{heat} \rightarrow CO + H_2$

$\{CH_2O\} + \text{heat} \rightarrow CO + H_2$

$CO + H_2O \rightarrow CO_2 + H_2$

$CO + 3H_2 \rightarrow CH_4 + H_2O$ (Methanation reaction)

$8CO + 17H_2 \rightarrow C_8H_{18} + 8H_2O$ (Fischer-Tropsch reaction)

18. What is a major proposed use of liquid methanol as a fuel for the future?

    Answer: Methanol can be broken down catalytically to generate hydrogen gas for fuel cells.

19. Describe a direct and an indirect way to produce electricity from solar energy.

    Answer: A direct way is with photovoltaic cells and an indirect way is to use concentrated solar energy to heat a working fluid in a heat engine coupled mechanically to an electrical generator.

20. What is the distinction between donor and acceptor layers in photovoltaic cells?

    Answer: The donor layer has loosely bound electrons that can be "donated" with photochemical energy and the acceptor layer has "holes" that accept the electrons.

21. Using internet resources for information list some possible means for storing energy generated from solar radiation?

    Answer: Some major possibilities for energy storage include high-capacity electrical batteries, flywheels, and pumped water storage for hydroelectric regeneration of electricity.

22. What are the advantages of *Pittsosporum reiniferum* and *Euphorbia lathyrus* for the production of biomass energy?

    Answer: Both of these plants produce hydrocarbons directly.

23. Corn produces biomass in large quantities during its growing season. What are two potential sources of biomass fuel from corn, one that depends upon the corn grain and the other that does not?

    Answer: One source of biomass fuel from corn is ethanol produced by the fermentation of glucose derived from corn grain starch. An alternative is to thermochemically gasify cornstalks and produce synthetic fuels from the gas generated.

24. Does the use of biomass for fuel contribute to greenhouse gas carbon dioxide? Explain.

    Answer: Biomass fuel is generally carbon dioxide-neutral in that the carbon dioxide released by the combustion of biofuels was previously removed from the atmosphere by photosynthesis.

25. What fermentation process is used to generate a fuel from wastes, such as animal wastes?

    Answer: The following anoxic process generates methane gas: $2\{CH_2O\} \rightarrow CH_4 + CO_2$

26. What are two potential pollution problems that accompany the use of geothermal energy to generate electricity?

    Answer: Two potential problems are release of toxic hydrogen sulfide gas and polluted water from some geothermal waters

27. What basic phenomenon is responsible for nuclear energy? What keeps the process going?

Answer: Fission of heavy nuclei, such as those of uranium or plutonium, releases heat utilized in nuclear energy. The process is kept going by the release of neutrons during fission which, in turn, cause other nuclear fissions in a chain reaction.

28. What is the biggest problem with nuclear energy? Why is it not such a bad idea to store spent nuclear fuel at a reactor site for a number of years before moving it?

    Answer: The biggest perceived problem with nuclear energy is dealing with the radioactive products of fission and radioactive elements, such as plutonium, produced when atomic nuclei absorb neutrons. The rate at which the radioactivity of fission products decreases is especially rapid in the first several years after they are produced, so simply leaving spent fuel at the reactor site results in a much decreased level of radioactivity that must eventually be handled.

29. What is meant by passive stability in nuclear reactor design?

    Answer: Passive stability refers to features that automatically shut a nuclear reactor down in the event of a malfunction without the need for measures such as pumping water into the system.

30. What is the status of thermonuclear fusion for power production?

    Answer: It has great promise because potentially the fuel is without limits and there are no radioactive fission products. However, to date a practical fusion power reactor has not been developed and after decades of failed attempts probably will never be.

31. Arrange the following energy conversion processes in order from the least to the most efficient: (A) electric hot water heater, (B) photosynthesis, (C) solar cell, (D) electric generator, (E) aircraft jet engine.

    Answer: B<C<E<D<A

32. Considering the Carnot equation and common means for energy conversion, what might be the role of improved materials (metal alloys, ceramics) in increasing energy conversion efficiency?

    Answer: Materials that resist high temperatures enable higher peak temperatures in heat engines leading to higher efficiencies.

33. As it is now used, what is the principle or basis for the production of energy from uranium by nuclear fission? Is this process actually used for energy production? What are some of its environmental disadvantages? What is one major advantage?

    Answer: Energy is released when uranium or plutonium nuclei undergo fission. A major disadvantage is production of radioactive fission products and a major advantage is that nuclear fission does not release greenhouse gas emissions.

34. What would be at least two highly desirable features of nuclear fusion power if it could ever be achieved in a controllable fashion on a large scale?

    Answer: Abundant fuel and lack of radioactive fission products.

35. Justify describing the sun as “an ideal energy source.” What are two big disadvantages of solar energy?

    Answer: Solar energy is ideal in that it is renewable, free, and essentially inexhaustible. Disadvantages include its intermittent nature and large land areas required for solar installations.

36. What are some of the greater implications of the use of biomass for energy? How might such widespread use affect greenhouse warming? How might it affect agricultural production of food?

    Answer: Biomass energy is a renewable resource. It potentially takes up large amounts of land. Much of the land used might be unsuitable for food crop production and highly productive algae can be grown in impoundments containing saline water and located in desert areas. Biomass energy is essentially greenhouse-gas-neutral; however, it can be used to replace fossil fuels that do emit large amounts of carbon dioxide to the atmosphere. Use of grain and food oils to make biofuels tends to have a negative effect on food production as would use of non-food biomass if crops are grown on land that otherwise could be employed for crop production.

37. On the internet look up the Bakken tight shale formation in North Dakota as an emerging source of petroleum. Was it producing any oil in 2000? What is its current rate of production? Why was it not developed earlier, such as during the first "energy crisis" in the 1970s?

    Answer: Production from the Bakken tight shale formation in North Dakota began with the discovery of the Parshall Oil Field in 2006, and peaked in 2012 with subsequent declining production due to low petroleum prices. Because of production from this formation, North Dakota advanced from about 8th in U. S. oil production to second, only trailing Texas. Various internet sites discuss a number of interesting aspects of the North Dakota "oil boom" including a sharp increase in the state's economic status as well as social, environmental, and infrastructure problems that have resulted from it. Although it was well known for decades that there were vast petroleum and natural gas resources in "tight" shale, it was only with the development of hydraulic fracturing techniques and horizontal drilling that it became possible to release these hydrocarbons from the shale formations,

38. From a search on the internet, look up the largest coal-based synthetic fuels plant in the U.S. Where is it located? What does it make? How long has it been operating? Get the same information for the largest coal-based synthetic fuel plant in the world. Is there at least one other synthetic fuels plant in the world that uses natural gas as a feedstock? What is the future of such plants given recent increased development of previously inaccessible natural gas resources?

    Answer: The Great Plains Synfuels Plant (GPSP) in Beulah, North Dakota is the only coal-to-synthetic natural gas plant in the U.S., beginning operation in 1984. It produces methane, ammonia, urea fertilizer, and byproduct carbon dioxide used for secondary petroleum recovery. The largest and longest operating such plant is in Sasol, South Africa, and has been in operation for several decades. The Middle Eastern country of Qatar has a large plant to produce hydrocarbon liquids from natural gas. The future of plants such as the one in Qatar is probably pretty bright given new methods of producing abundant supplies of natural gas.

39. What was "cold fusion" energy generation supposed to do? When and where was it announced? Why has it been characterized "one of the greatest scientific embarrassments of modern times"?

    Answer: Announced with much publicity by chemists Martin Fleischmann of the University of Southampton and Stanley Pons of the University of Utah in 1989, "cold fusion" of deuterium nuclei was described as occurring at a palladium electrode during the electrolysis of heavy water (deuterium oxide) and was publicized as a possible energy panacea. Subsequent investigations failed to verify the cold fusion phenomenon and it has no credible

theoretical basis, although investigations have continued by "believers" even to the present day.

Chapter 19
The Nature, Sources, and Environmental Chemistry of Hazardous Wastes

1. Match each of the following kinds of hazardous substances on the left with a specific example of each from the right, below:

   (1) Explosives (A) Oleum, sulfuric acid, caustic soda

   (2) Compressed gases (B) White phosphorus

   (3) Radioactive materials (C) NH_4ClO_4

   (4) Flammable solids (D) Hydrogen, sulfur dioxide

   (5) Oxidizing materials (E) Nitroglycerin

   (6) Corrosive materials (F) Plutonium, cobalt-60

   Answer: (1)-(E), (2)-(D), (3)-(F), (4)-(B), (5)-(C), (6)-(A)

2. Of the following, the property that is **not** a member of the same group as the other properties listed is (A) substances that are liquids whose vapors are likely to ignite in the presence of ignition sources, (B) non-liquids that may catch fire from friction or contact with water and which burn vigorously or persistently, (C) ignitable compressed gases, (D) oxidizers, (E) substances that exhibit extremes of acidity or basicity.

   Answer: (E), Substances that exhibit extremes of acidity or basicity are corrosive substances and need not be flammable or oxidizers

3. In what respects may it be said that measures taken to alleviate air and water pollution tend to aggravate hazardous waste problems?

   Answer: Air and water pollutants collected prior to release are generally hazardous and become hazardous wastes when placed in the environment.

4. Why is attenuation of metals likely to be very poor in acidic leachate? Why is attenuation of anionic species in soil less than that of cationic species?

   Answer: Most metals are in solution as cationic species, such as Pb^{2+}, and in acidic leachate the H^+ ion competes with these metals for sites that bind cations to mineral surfaces. Anionic species are poorly attenuated by soils because of the lack of anion-exchanging sites on soil surfaces.

5. Discuss the significance of LFL, UFL, and flammability range in determining the flammability hazards of organic liquids.

   Answer: Substances with a relatively low LFL and a high UFL, hence a large flammability range tend to pose relatively greater flammability hazards.

6. Concentrated HNO_3 and its reaction products pose several kinds of hazards. What are these?

   Answer: Concentrated HNO_3 is a corrosive oxidant and is very damaging to flesh. One of its major reaction products, NO_2, is quite toxic when inhaled and can cause death.

7. What are substances called that catch fire spontaneously in air without an ignition source?

   Answer: Pyrophoric substances can catch fire spontaneously without an ignition source and

present dangerous fire hazards.

8. Name four or five hazardous products of combustion and specify the hazards posed by these materials.

   Answer: CO from incomplete combustion of carbonaceous fuels and HCN from combustion of some nitrogen-containing compounds are toxic and can be fatal. SO_2 evolved from combustion of organosulfur compounds is an air pollutant. Polycyclic aromatic compounds from incomplete combustion of organic compounds can be carcinogenic (benzo(a)pyrene is the main example).

9. What kind of property tends to be imparted to a functional group of an organic compound containing both oxygen and nitrogen?

   Answer: This kind of functionality causes compounds to be reactive and in many cases explosive.

10. Match the corrosive substance from the column on the left, below, with one of its major properties from the right column:

(1) Alkali metal hydroxides	(A) Oxidizer
(2) Hydrogen peroxide	(B) Strong bases
(3) Hydrofluoric acid, HF	(C) Dissolves glass
(4) Nitric acid, HNO_3	(D) Reacts with tissue to form yellow xanthoproteic acid

   Answer: 1-B, 2-A, 3-C, 4-D

11. Rank the following wastes in increasing order of segregation (A) mixed halogenated and hydrocarbon solvents containing little water, (B) spent steel pickling liquor, (C) dilute sludge consisting of mixed organic and inorganic wastes, (D) spent hydrocarbon solvents free of halogenated materials, (E) dilute mixed inorganic sludge.

   Answer: C (least segregated), A and E, B and D (most segregated)

12. Inorganic species may be divided into three major groups based upon their retention by clays. What are the elements commonly listed in these groups? What is the chemical basis for this division? How might anions (Cl^-, NO_3^-) be classified?

   Answer: Elements that tend to be highly retained by clay include cadmium, mercury, lead, and zinc. Potassium, magnesium, iron, silicon, and NH_4^+ ions are moderately retained by clay, whereas sodium, chloride, calcium, manganese, and boron ions are poorly retained. The retention of the last three elements is probably biased in that they are leached from clay, so that negative retention (elution) is often observed. Since clays do not possess anion exchange sites, it is likely that anions would be very poorly retained.

13. In what form would a large quantity of hazardous waste PCB likely be found in the hydrosphere?

   Answer: PCB compounds are generally high-density liquids that are insoluble in water, so a mass of PCB waste would likely be in a pool at the bottom of a lake or in a stream bed.

14. The Toxicity Characteristic Leaching Procedure was originally devised to mimic a "mismanagement scenario" in which hazardous wastes were disposed along with biodegradable organic municipal refuse. Discuss how this procedure reflects the conditions that might arise from circumstances in which hazardous wastes and actively decaying municipal refuse were disposed together.

   Answer: This procedure is based upon extraction of specific hazardous substances by a

buffered weak acid solution. Anoxic decay of organic matter in a waste site generally produces a weakly acidic leachate that will tend to leach hazardous substances co-disposed with the waste.

15. What are three major properties of wastes that determine their amenability to transport?

    Answer: The major physical properties of wastes that determine their amenability to transport are volatility, solubility, and the degree to which they are sorbed to solids, including soil and sediments.

16. List and discuss the significance of major sources for the origin of hazardous wastes, that is, their main modes of entry into the environment. What are the relative dangers posed by each of these? Which part of the environment would each be most likely to contaminate?

    Answer: In the past, hazardous substances have been deliberately added to the environment by humans. Wastewater containing a variety of toxic substances has been discharged in large quantities into waterways. Hazardous gases and particulate matter have been discharged into the atmosphere through stacks from power plants, incinerators, and a variety of industrial operations. Hazardous wastes have been deliberately spread on soil or placed in landfills in the geosphere. Evaporation and wind erosion may move hazardous materials from wastes dumps into the atmosphere, or they may be leached from waste dumps into groundwater or surface waters. Underground storage tanks or pipelines have leaked a variety of materials into soil. Accidents, fires, and explosions may distribute dangerous materials into the environment. Another source of such materials consists of improperly operated waste treatment or storage facilities.

17. What is the influence of organic solvents in leachates upon attenuation of organic hazardous waste constituents?

    Answer: Organic solvents in leachates tend to keep organic hazardous waste constituents in solution and prevent their attenuation by mineral solids.

18. What features or characteristics should a compound possess in order for direct photolysis to be a significant factor in its removal from the atmosphere?

    Answer: A chromophore that can absorb a photon.

19. Describe the particular danger posed by codisposal of strong chelating agents with radionuclide wastes. What may be said about the chemical nature of the latter with regard to this danger?

    Answer: Strong chelating agents bind with chelatable metal radionuclides thus facilitating their transport through soil and mineral formations.

20. Describe a beneficial effect that might result from the precipitation of either $Fe_2O_3 \cdot xH_2O$ or $MnO_2 \cdot xH_2O$ from hazardous wastes in water.

    Answer: These solids have strong tendencies to sequester heavy metals and remove them from water solution.

21. Why are secondary air pollutants from hazardous waste sites usually of only limited concern as compared to primary air pollutants? What is the distinction between the two?

    Answer: Primary air pollutants are those that are pollutants in the forms in which they are released. Secondary air pollutants are formed by atmospheric chemical reactions of substances emitted to the atmosphere. In extreme cases, primary air pollutants emitted from hazardous waste sites can cause rather bad localized air pollution conditions. Secondary air pollutants usually form some distance from the origin of their parent materials and are diluted

during transport, therefore posing relatively less hazard from hazardous waste sites.

22. Match the following physical, chemical, and biochemical processes dealing with the transformations and ultimate fates of hazardous chemical species in the hydrosphere on the left with the description of the process on the right, below:

(1) Precipitation reactions	(A) Molecule is cleaved with the addition of H_2O
(2) Biochemical processes	(B) Often involve hydrolysis and oxidation-reduction
(3) Oxidation-reduction	(C) By sediments and by suspended matter
(4) Hydrolysis reactions	(D) Generally mediated by microorganisms
(5) Sorption	(E) Generally accompanied by aggregation of colloidal particles suspended in water

Answer: (1)-(E), (2)-(B), (3)-(D), 4-(A) 5-(C)

23. As applied to hazardous wastes in the biosphere, distinguish among biodegradation, biotransformation, detoxification, and mineralization.

Answer: Biodegradation is the biologically-mediated breakdown of organic wastes which, if it proceeds all the way to simple inorganic species, is classified as mineralization. Biotransformation is the biologically-mediated alteration of a waste compound, in some cases to even a more toxic form. Detoxification is conversion of a toxic substance to one that is not toxic.

24. What is the potential role of *Phanerochaete chrysosporium* (white rot fungus) in treatment of hazardous waste compounds? For which kinds of compounds might it be most useful?

Answer: This organism can break down hazardous waste compounds. It is particularly useful for those compounds, such as PCBs, that are normally considered to be refractory.

25. Which part of the hydrosphere is most subject to long-term, largely irreversible contamination from the improper disposal of hazardous wastes in the environment?

Answer: Groundwater

26. Several physical and chemical characteristics are involved in determining the amenability of a hazardous waste compound to biodegradation. These include hydrophobicity, solubility, volatility, and affinity for lipids. Suggest and discuss ways in which each one of these factors might affect biodegradability.

Answer: Hydrophobicity is usually a characteristic of a substance that has a strong affinity for lipids. Such substances have a tendency to bioaccumulate in the lipid tissue of organisms and can be detrimental to biodegradation. Relatively soluble substances can be ingested by organisms thus facilitating biodegradation. More volatile compounds tend to be removed from the vicinity of biodegrading organisms which can be detrimental to biodegradation.

27. List and discuss some of the important processes determining the transformations and ultimate fates of hazardous chemical species in the hydrosphere.

Answer: Once in the hydrosphere, hazardous waste species can undergo a number of processes by which they are degraded, retained, and transformed. These include the common chemical processes of precipitation-dissolution, acid-base reactions, hydrolysis, and oxidation-reduction reactions. Also included are a wide variety of biochemical processes which, in most cases, reduce hazards, but in some cases, such as the biomethylation of mercury, greatly increase the risks posed by hazardous wastes.

Chapter 20
Industrial Ecology for Waste Minimization, Utilization, and Treatment

1. Place the following in descending order of desirability for dealing with wastes and discuss your rationale for doing so (explain): (A) reducing the volume of remaining wastes by measures such as incineration, (B) placing the residual material in landfills, properly protected from leaching or release by other pathways, (C) treating residual material as much as possible to render it nonleachable and innocuous, (D) reduction of wastes at the source, (E) recycling as much waste as is practical.

   Answer: D>E>A>C>B

2. Match the waste recycling process or industry from the column on the left with the kind of material that can be recycled from the list on the right, below:

   (A) Recycle as raw material to the generator
   (B) Utilization for pollution control or waste treatment
   (C) Energy production
   (D) Materials with agricultural uses
   (E) Organic substances

   (1) Waste alkali
   (2) Hydraulic and lubricating oils
   (3) Incinerable materials
   (4) Incompletely consumed feedstock material
   (5) Waste lime or phosphate-containing sludge

   Answer: (A)-(4), (B)-(1), (C)-(2) and (3), (D)-(5), (E)-(2) and (3)

3. What material is recycled using hydrofinishing, treatment with clay, and filtration?

   Answer: Formerly used for waste motor oil

4. What is the "most important operation in solvent purification and recycle" that is used to separate solvents from impurities, water, and other solvents?

   Answer: Fractional distillation

5. Dissolved air flotation (DAF) is used in the secondary treatment of wastes. What is the principle of this technique? For what kinds of hazardous waste substances is it most applicable?

   Answer: DAF injects water saturated with high-pressure air into the bottom of a treatment tank. Air that comes out of solution as the pressure is released forms small bubbles that attach to small particles and float them to the top of the tank where they can be skimmed off. The technique is especially applicable to the treatment of colloidal organic impurities in water.

6. Match the process or industry from the column on the left with its "phase of waste treatment" from the list on the right, below:

   (A) Activated carbon sorption
   (B) Precipitation
   (C) Reverse osmosis
   (D) Emulsion breaking
   (E) Slurrying

   (1) Primary treatment
   (2) Secondary treatment
   (3) Polishing

Answer: (A)-(3), (B)-(2), (C)-(3), (D)-(2), (E)-(1)

7. Distillation is used in treating and recycling a variety of wastes, including solvents, waste oil, aqueous phenolic wastes, and mixtures of ethylbenzene and styrene. What is the major hazardous waste problem that arises from the use of distillation for waste treatment?

   Answer: Distillation bottoms, residues from the distillation process that may become hazardous wastes.

8. Supercritical fluid technology has a great deal of potential for the treatment of hazardous wastes. What are the principles involved with the use of supercritical fluids for waste treatment? Why is this technique especially advantageous? Which substance is most likely to be used as a supercritical fluid in this application? For which kinds of wastes are supercritical fluids most useful?

   Answer: A supercritical fluid is one that has characteristics of both liquid and gas and consists of a substance above its critical temperature and pressure (31.1°C and 73.8 atm, respectively, for CO_2). A major advantage of supercritical fluid extraction is that after a substance has been extracted from a waste into a supercritical fluid at high pressure, the pressure can be released, resulting in separation of the substance extracted. The fluid can then be compressed again and recirculated through the extraction system. The fluid most commonly used in supercritical fluid extraction is supercritical CO_2. Some possibilities for treatment of hazardous wastes by extraction with supercritical CO_2 include removal of organic contaminants from wastewater, extraction of organohalide pesticides from soil, extraction of oil from emulsions used in aluminum and steel processing, and regeneration of spent activated carbon.

9. What are some advantages of using acetic acid, compared, for example, to sulfuric acid, as a neutralizing agent for treating waste alkaline materials?

   Answer: Acetic acid is a weak acid and less hazardous to use than sulfuric acid. It is also biodegradable and can be made by fermentation of renewable biomass.

10. Designate which of the following would be **least likely** to be produced by, or used as a reagent for the removal of heavy metals by their precipitation from solution (explain): (A) Na_2CO_3, (B) CdS, (C) $Cr(OH)_3$, (D) KNO_3, (E) $Ca(OH)_2$

    Answer: (D), KNO_3 would not precipitate heavy metals

11. Both $NaBH_4$ and Zn are used to remove metals from solution. How do these substances remove metals? What are the forms of the metal products?

    Answer: Both of these reagents are reducing agents that reduce metal ions such as Pb^{2+} and Cd^{2+} to the solid metal that can be reclaimed.

12. Of the following, thermal treatment of wastes is **not** useful for (explain): (A) Volume reduction, (B) Destruction of heavy metals, (C) removal of volatile, combustible, mobile organic matter, (D) destruction of pathogenic materials, (E) destruction of toxic substances.

    Answer: (B) Heavy metals are not destroyed by thermal treatment.

13. From the following, choose the waste liquid that is least amenable to incineration and explain why it is not readily incinerated: (A) Methanol, (B) tetrachloroethylene, (C) acetonitrile, (D) toluene, (E) ethanol, (F) acetone.

    Answer: (B) Tetrachloroethylene is difficult to burn and produces acidic HCl as a waste byproduct.

14. Name and give the advantages of the process that is used to destroy more hazardous wastes

by thermal means than are burned solely for the purpose of waste destruction.

Answer: Large quantities of hazardous wastes are destroyed by cement manufacture where the high-temperature oxidizing conditions are ideal for destroying organic wastes and the alkaline mineral slag sequesters acid gases and binds heavy metals.

15. What is the major advantage of fluidized-bed incinerators from the standpoint of controlling pollutant byproducts?

    Answer: A fluidized bed incinerator employs a bed of granular alkaline material that sequesters acid gas products such as HCl in the combustion chamber.

16. Explain the best way to obtain microorganisms to be used in the treatment of hazardous wastes by biodegradation?

    Answer: Such microorganisms are best obtained from soil at a site contaminated by the kinds of wastes to be degraded.

17. What are the principles of composting? How is it used to treat hazardous wastes?

    Answer: Composting utilizes a population of microorganisms held by a porous support, such as sawdust, to provide contact with air that the microorganisms require for the biodegradation to occur. Hazardous waste materials are mixed with the support material which is periodically stirred (turned) to facilitate mixing and exposure to air.

18. How is portland cement used in the treatment of hazardous wastes for disposal? What might be some disadvantages of such a use?

    Answer: Portland cement is used to bind with and solidify such wastes. Particularly with organic wastes, the solidified cement product may lack physical integrity and the cement adds a lot to the bulk of the waste.

19. What are the advantages of aboveground disposal of hazardous wastes as opposed to burying wastes in landfills?

    Answer: The most important advantage is that it avoids infiltration by groundwater that can result in leaching and groundwater contamination common to storage in pits and landfills.

20. Describe and explain the best approach to managing leachate from hazardous waste disposal sites.

    Answer: The best approach to leachate management is to prevent its production by limiting infiltration of water into the site.

21. An incinerator is operated primarily to destroy chlorophenols as the principal organic hazardous constituents (POHC) fed along with other less hazardous constituents at an average rate of 10 kg/hour. The exhaust gas coming from the incinerator stack at a rate of 10 m^3/min contains 1 microgram/m^3 of chlorophenols. What is the DRE of the incinerator for the POHC?

    Answer: In 1 hour the output of chlorophenols in the exhaust is

$$\frac{60\ \text{minutes}}{\text{hour}} \times \frac{10\ \text{m}^3}{\text{min}} \times \frac{1\times10^{-9}\ \text{kg}}{\text{m}^3} = \frac{6\times10^{-7}\ \text{kg}}{\text{hour}}$$

$$\text{DRE} = \frac{10-(6\times10^{-7})}{10}\times100 = 99.999994\%$$

22. Can phytoremediation be described as a bioremediation process? Is it a biodegradation process? If not, how can it be used to treat hazardous wastes?

    Answer: Phytoremediation uses plants to remove wastes from below ground and collect the

waste material in plant biomass. Normally, biodegradation does not occur with phytoremediation, but it is used to collect and concentrate wastes that can then be destroyed by processes such as incineration of the plant biomass.

Chapter 21
The Biosphere: Environmental Biochemistry

1. What is the toxicological importance of lipids? How are lipids related to hydrophobic pollutants and toxicants?

   Answer: Lipids serve as reservoirs for the bioaccumulation of poorly water-soluble, lipophilic toxicants and pollutants. Those that are hydrophobic tend to accumulate in lipids.

2. What is the function of a hydrolase enzyme?

   Answer: A hydrolase enzyme breaks a molecule into two parts with insertion of H_2O.

3. Match the cell structure on the left with its function on the right, below:

(1) Mitochondria	(A) Toxicant metabolism
(2) Endoplasmic reticulum	(B) Fills the cell
(3) Cell membrane	(C) Deoxyribonucleic acid
(4) Cytoplasm	(D) Mediate energy conversion and utilization
(5) Cell nucleus	(E) Encloses the cell and regulates the passage of materials into and out of the cell interior

   Answer: (1)-(D), (2)-(A), (3)-(E), (4)-(B), (5)-(C)

4. The formula of simple sugars is $C_6H_{12}O_6$. The simple formula of higher carbohydrates is $C_6H_{10}O_5$. Of course, many of these units are required to make a molecule of starch or cellulose. If higher carbohydrates are formed by joining together molecules of simple sugars, why is there a difference in the ratios of C, H, and O atoms in the higher carbohydrates as compared to the simple sugars?

   Answer: The reaction for forming a disaccharide from two simple sugars is

   $2C_6H_{12}O_6 \rightarrow C_{12}H_{22}O_{11} + H_2O$

   As more simple sugar units are joined to produce larger carbohydrate molecules including starch and cellulose, each bonding accompanied by a loss of H_2O, the simple formula approaches $C_6H_{10}O_5$.

5. Why does wood contain so much cellulose ($C_{600}H_{1000}O_{500}$)?

   Answer: Cellulose is a structural material which, along with lignin, composes the mass of wood and gives it strength.

6. What would be the chemical formula of a *tri*saccharide made by the bonding together of three simple sugar molecules?

   Answer: $C_{18}H_{32}O_{16}$

7. The general formula of cellulose may be represented as $(C_6H_{10}O_5)_x$. If the molar mass of a molecule of cellulose is 400,000, what is the estimated value of *x*?

   Answer: The molar mass of each unit of $C_6H_{10}O_5$ is 162. Therefore,

   X = 400,000/162 = 2469

8. During one month a factory for the production of simple sugars, $C_6H_{12}O_6$, by the hydrolysis

of cellulose processes one million pounds of cellulose. The percentage of cellulose that undergoes the hydrolysis reaction is 40%. How many pounds of water are consumed in the hydrolysis of cellulose each month?

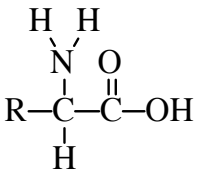
Answer: The chemical reaction for processing cellulose by hydrolysis into a simple sugar is $(C_6H_{10}O_5)_x + xH_2O \rightarrow xC_6H_{12}O_6$, which for stoichiometric purposes can be simplified to $C_6H_{10}O_5 + H_2O \rightarrow C_6H_{12}O_6$. Since only 40% of the cellulose undergoes hydrolysis, 400,000 lbs cellulose (abbreviated cel) is converted to sugar each month or 1.814×10^8 g of cel/month. Using the simplified formula the molar mass of $C_6H_{10}O_5$ = 162 g/mol

$$\text{Mass } H_2O = 1.814 \times 10^8 \text{ g cel} \times \frac{1 \text{ mol cel}}{162 \text{ g cel}} \times \frac{1 \text{ mol } H_2O}{\text{mol cel}} \times \frac{18 \text{ g } H_2O}{\text{mol } H_2O} = 2.01 \times 10^7 \text{ g } H_2O$$

$$\text{Mass } H_2O \text{ (lb)} = 4.43 \times 10^4 \text{ lb } H_2O = 44{,}300 \text{ lb } H_2O$$

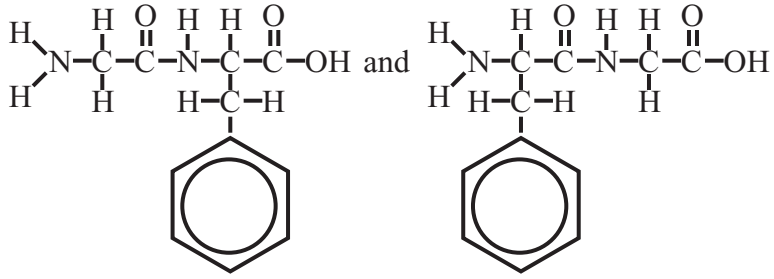
9. What is the structure of the largest group of atoms common to all amino acid molecules?

Answer:



10. Glycine and phenylalanine can join together to form two different dipeptides. What are the structures of these two dipeptides?

Answer:



11. One of the ways in which two parallel protein chains are joined together, or cross-linked, is by way of an —S—S— link. What amino acid to you think might be most likely to be involved in such a link? Explain your choice.

Answer: The amino acid would be cysteine, which has the -SH group capable of forming the required –S–S– links.

12. Fungi, which break down wood, straw, and other plant material, have what are called "exoenzymes." Fungi have no teeth and cannot break up plant material physically by force. Knowing this, what do you suppose an exoenzyme is? Explain how you think it might operate in the process by which fungi break down something as tough as wood.

Answer: An exoenzyme operates outside the body of an organism. Fungi excrete exoenzymes that break down plant material to soluble forms that can be absorbed by the fungi (cellulose to soluble glucose sugar).

13. Many fatty acids of lower molecular weight have a bad odor. Speculate as to the reasons that rancid butter has a bad odor. What chemical compound is produced that has a bad odor? What sort of chemical reaction is involved in its production?

Answer: Rancid butter has a bad odor due to the production of odorous butyric acid that is produced when the triglyceride that composes the fat in butter is hydrolyzed biochemicalliy.

14. The long-chain alcohol with 10 carbons is called decanol. What do you think would be the formula of decyl stearate? To what class of compounds would it belong?

    Answer: The formula for decanol would be $HO(CH_2)_9CH_3$ and that of stearic acid would be $CH_3(CH_2)_{16}COOH$ making the formula of decyl stearate $CH_3(CH_2)_{16}C(O)O(CH_2)_9CH_3$.

15. Write an equation for the chemical reaction between sodium hydroxide and cetyl stearate. What are the products?

    Answer: The reaction would be the following in which the products are cetyl alcohol and sodium stearate:

    $CH_3(CH_2)_{15}O(O)C(CH_2)_{16}CH_3 + NaOH \rightarrow CH_3(CH_2)_{15}OH + Na^{+-}O_2C(CH_2)_{16}CH_3$

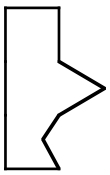
16. What type of endocrine gland is found only in females? What type of these glands is found only in males?

    Answer: Ovaries occur only in females and testes only in males.

17. The action of bile salts is a little like that of soap. What function do bile salts perform in the intestine? Look up the action of soaps in Chapter 5, and explain how you think bile salts may function somewhat like soap.

    Answer: Bile salts would be expected to form micelles that suspend very small globules of fats or oils making them accessible to enzyme action.

18. If the structure of an enzyme is illustrated as,



how should the structure of its substrate be represented?

Answer: **Enzyme showing shape of active site**

Substrate with structural feature fit by enzyme active site

19. Look up the structures of ribose and deoxyribose. Explain where the "deoxy" came from in the name deoxyribose.

    Answer: Deoxyribose is missing one of the O atoms present in ribose.

20. In what respect is an enzyme and its substrate like two opposite strands of DNA?

    Answer: Like two opposite strands of DNA, an enzyme and its substrate fit together like a "lock and key."

21. For what discovery are Watson and Crick noted?

    Answer: Watson and Crick are noted for figuring out the double helix structure of DNA (see Figures 21.12 and 21.13).

22. Why does an enzyme no longer function if it is denatured?

    Answer: The shape of the active site is altered when an enzyme is denatured so that it no longer fits the substrate upon which it was intended to act.

Chapter 22
Toxicological Chemistry

1. How are conjugating agents and Phase II reactions involved with some toxicants?

   Answer: Phase II reactions are those in which conjugating agents are attached to xenobiotic substances or their metabolites, generally making these products more water-soluble and readily eliminated from the body, but in some cases more toxic.

2. What is the toxicological importance of proteins, particularly as related to protein structure?

   Answer: Proteins are subject to damaging alteration by toxicants. When the protein structure is altered (denatured) the protein may no longer serve its intended purpose.

3. What is the toxicological importance of lipids? How are lipids related to hydrophobic pollutants and toxicants?

   Answer: Toxicants may alter the metabolism of lipids causing harmful effects such as accumulation of lipids in the liver (fatty liver). A second effect of lipids is the accumulation of hydrophobic persistent compounds in lipid tissue.

4. What are Phase 1 reactions? What enzyme system carries them out? Where is this enzyme system located in the cell?

   Answer: Phase 1 reactions on xenobiotic compounds make them more water-soluble and reactive by the attachment of polar functional groups, such as –OH. Most Phase 1 processes are "microsomal mixed-function oxidase" reactions catalyzed by the cytochrome P-450 enzyme system. associated with the **endoplasmic reticulum** of the cell and occurring most abundantly in the liver of vertebrates.

5. Name and describe the science that deals with the chemical nature and reactions of toxic substances, including their origins, uses, and chemical aspects of exposure, fates, and disposal.

   Answer: The science is toxicological chemistry, which is pretty well summarized in the statement of this question and is described in detail in this chapter.

6. What is a dose-response curve?

   Answer: A dose-response curve is a plot of the percentage of individuals exhibiting a particular response (especially death) as a function of dose; it is generally an S-shaped curve.

7. What is meant by a toxicity rating of 6?

   Answer: A substance with a toxicity rating of 6 is "supertoxic." The incredibly toxic botulinus toxin is an example.

8. What are the three major subdivisions of the *dynamic phase* of toxicity, and what happens in each?

   Answer: The dynamic phase is divided among (1) a primary reaction with a receptor or target organ, such as binding of a toxicant to an enzyme; (2) a biochemical response, such as prevention of an enzyme from acting; and (3) an observable effect, such as alteration of

vital signs.

9. Characterize the toxic effect of carbon monoxide in the body. Is its effect reversible or irreversible? Does it act on an enzyme system?

   Answer: Carbon monoxide bonds strongly, but reversibly, with blood hemoglobin so that the hemoglobin is ineffective in carrying oxygen from the lungs to body tissues leading to asphyxiation. The binding is non-enzymatic.

10. Of the following, choose the one that is **not** a biochemical effect of a toxic substance (explain): (A) impairment of enzyme function by binding to the enzyme, (B) alteration of cell membrane or carriers in cell membranes, (C) change in vital signs, (D) interference with lipid metabolism, (E) interference with respiration.

    Answer: C is an observable effect, not a biochemical action.

11. Distinguish among teratogenesis, mutagenesis, carcinogenesis, and immune system effects. Are there ways in which they are related?

    Answer: Teratogenesis refers to damage to progeny from toxicants. Mutagenesis occurs when DNA is altered leading to altered, potentially inheritable traits. Carcinogenesis commonly occurs by the same mechanism as mutagenesis leading to uncontrolled cell replication (cancer). Immune system effects occur when xenobiotic substances either make the immune system hypersensitive or repress it. Often these different effects are closely related as is the case with the connection between mutagenesis and carcinogenesis. Alteration of DNA can cause teratogenesis.

12. As far as environmental toxicants are concerned, compare the relative importance of acute and chronic toxic effects and discuss the difficulties and uncertainties involved in studying each.

    Answer: Acute effects are easier to observe and study. However, particularly in the case of long-term environmental exposure to toxicants, chronic effects generally cause more harm, but are relatively more difficult to study because of factors that include long time periods before effects are observed, subtle nature of some effects, and difficulty in establishing cause and effect.

13. What are some of the factors that complicate epidemiologic studies of toxicants?

    Answer: Epidemiologic studies are complicated by long latency periods from exposure to onset of disease, lack of specificity in the correlation between exposure to a particular agent and the occurrence of a disease, and background levels of a disease in the absence of exposure to an agent capable of causing the disease.

14. Alkylating agents do not or are not (explain): (A) formed by metabolic activation, (B) attach groups such as CH_3 to DNA, (C) include some species that cause cancer, (D) alter DNA, (E) noted for being electron-pair donors or nucleophiles.

    Answer: Alkylation occurs by way of generation of positively charged electrophilic species that bond to electron-rich nitrogen or oxygen atoms on the nitrogenous bases in DNA. They are electron-pair acceptors, not doners, so the correct answer is E.

15. Of the following, if any, the **untrue** statement regarding Phase 1 reactions is (explain): (A) they tend to introduce reactive, polar functional groups onto lipophilic ("fat-seeking") toxicant molecules, (B) the product of a Phase 1 reaction is usually more water-soluble than the parent xenobiotic species, (C) the product of a Phase1 reaction possesses a "chemical handle" to which a substrate material in the body may become attached so that the toxicant can be eliminated from the body, (D) Phase 1 reactions are generally conjugation reactions

through which an endogenous conjugating agent is attached, (E) Phase 1 reactions are catalyzed by enzymes.

Answer: The correct answer is D because this choice actually describes Phase 2 reactions.

Chapter 23
Toxicological Chemistry of Chemical Substances

1. List and discuss two elements that are invariably toxic in their elemental forms. For another element, list and discuss two elemental forms, one of which is quite toxic and the other of which is essential for the body. In what sense is even the toxic form of this element "essential for life?"

   Answer: Elemental chlorine, Cl_2, is a corrosive poison when it contacts skin and particularly pulmonary tissue. Elemental mercury is quite toxic when inhaled, although contact of liquid mercury metal with skin causes no harm. Elemental oxygen in the form of O_2 gas is essential for human respiration, whereas ozone, O_3, is toxic. However, ozone in the stratosphere is essential for life on Earth because of its capability to filter out ultraviolet radiation from the sun.

2. What is a toxic substance that bonds to iron(III) in iron-containing ferricytochrome oxidase enzyme, preventing its reduction to iron(II) in the oxidative phosphorylation process by which the body utilizes O_2?

   Answer: Cyanide in the form of HCN or cyanide ion, CN^-.

3. What are interhalogen compounds, and which elemental forms do their toxic effects most closely resemble?

   Answer: Interhalogen compounds are those composed of two different halogens, including ClF, BrCl, and BrF_3. The toxic effects of interhalogen compounds closely resemble those of the elemental halogens; these compounds are extremely reactive and are potent oxidants.

4. Name and describe the three health conditions that may be caused by inhalation of asbestos.

   Answer: Inhalation of asbestos may cause asbestosis (a pneumonia condition), mesothelioma (tumor of the mesothelial tissue lining the chest cavity adjacent to the lungs), and bronchogenic carcinoma (cancer originating with the air passages in the lungs).

5. Why might tetraethyllead be classified as "the most notable toxic organometallic compound"?

   Answer: Tetraethyllead may earn such a description because of its former widespread use as an octane booster in gasoline.

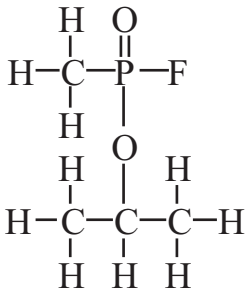
6. What is the most common toxic effect commonly attributed to low-molar-mass alkanes?

   Answer: Simple asphyxiation due to absence of O_2 in air that contains high levels of gaseous lower alkanes, such as methane, CH_4.

7. Information about the toxicities of many substances to humans is lacking because of limited data on direct human exposure. (Volunteers to study potentially fatal human health effects of toxicants are in notably short supply.) However, there is a great deal of information available about human exposure to phenol and the adverse effects of such exposure. Explain.

   Answer: Phenol was the first effective antiseptic known, and it was used directly upon human tissue to prevent infections from bacteria. As a consequence of this widespread use, many people were poisoned by phenol, in some cases resulting in death.

8. Comment on the toxicity of the compound below:



Answer: This compound is Sarin, a military poison nerve gas, a systemic poison to the central nervous system and acetylcholinesterase inhibitor that is readily absorbed as a liquid through the skin, Sarin may be lethal at doses as low as about 0.0l mg/kg; a single drop can kill a human.

9. What are neuropathic disorders? Why are organic solvents frequently the cause of such disorders?

Answer: Neuropathic disorders are disorders of nerve tissue. Exposure to organic solvents such as *n*-hexane and cyclohexane results in loss of myelin (a fatty substance constituting a sheath around certain nerve fibers) and degeneration of axons (part of a nerve cell through which nerve impulses are transferred out of the cell). This has resulted in multiple disorders of the nervous system (polyneuropathy) including muscle weakness and impaired sensory function of the hands and feet.

10. What is a major metabolic effect of aniline? What is this effect called? How is it manifested?

Answer: Metabolically, aniline converts iron(II) in hemoglobin to iron(III). This causes a condition called methemoglobinemia, characterized by cyanosis and a brown-black color of the blood, in which the hemoglobin can no longer transport oxygen in the body.

11. What are the organic compounds characterized by the N–N=O functional group? What is their major effect on health?

Answer: Compounds with this functional group are N-nitroso compounds, also called nitrosamines. Some of these compounds are carcinogens.

12. What structural group is characteristic of carbamates? For what purpose are these compounds commonly used? What are their major advantages in such an application?

Answer: The functional group below is characteristic of carbamates. These compounds are used as pesticides, particularly insecticides. Their advantages include relatively low toxicity to mammals and good biodegradability.

13. What is lipid peroxidation? Which common toxic substance is known to cause lipid peroxidation?

Answer: Lipid peroxidation occurs when the C=C double bonds in unsaturated body lipids are attacked by free radicals and undergo chain reactions in the presence of O_2, resulting in their oxidative destruction. Carbon tetrachloride, CCl_4, is notable for causing lipid peroxidation.

14. Biochemically, what do organophosphate esters such as parathion do that could classify them as “nerve poisons”?

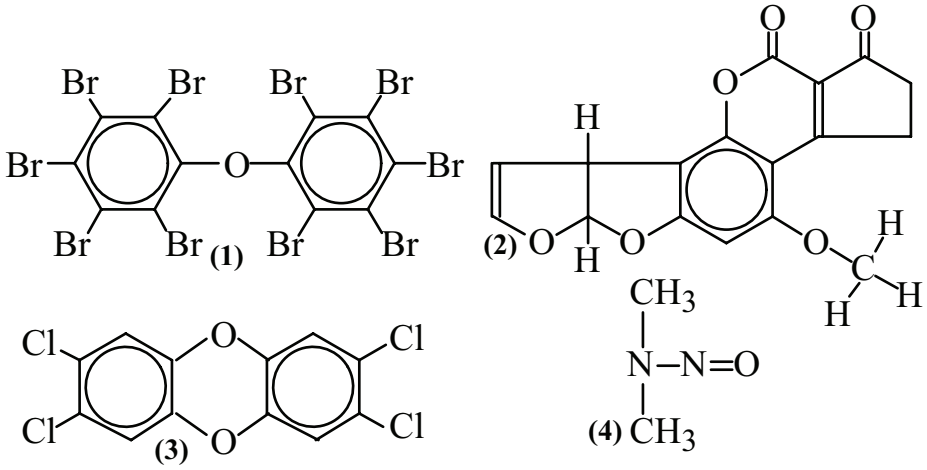
Answer: Some organophosphate esters inhibit acetylcholinesterase, an enzyme required to

stop transmission of nerve signals, a potentially fatal effect.

15. Although benzene and toluene have a number of chemical similarities, their metabolisms and toxic effects are quite different. Explain.

    Answer: The biochemical action on both of these compounds involves addition of oxygen. In the case of benzene, there is no choice other than attack on the aromatic ring. This results in biochemically reactive intermediates that react with biomolecules in the body and cause toxic effects, most notably leukemia from benzene exposure. Toluene has a methyl group attached to its aromatic ring and this methyl group reacts enzymatically with oxygen leading to the formation of benzoic acid (a common intermediate in the metabolism of some foods) and formation of hippuric acid, which is readily eliminated from the body with urine.

16. Match each compound in the figure below with its description from the following and explain your choices: (A) Byproduct of herbicide manufacture, (B) produced by fungi, (C) carcinogen, (D) though potentially a toxic pollutant, it has been difficult to find good substitutes for its use.



    Answer: (A)-(3), (B)-(2), (C)-(4), (D)-(1)

17. Consider three substances mentioned in this chapter, "A, B, C, and D," that are toxic because they interfere with oxygen transport or utilization in the body. A does not affect hemoglobin, but it can result in asphyxiation. B and C prevent hemoglobin from transporting O_2. Toxic substance D prevents the body from utilizing O_2 in metabolic processes. Because D has an affinity for a metal ion in a particular oxidation state, C can actually act as an antidote to poisoning from D. Give plausible identities of these four species and explain your choice in detail.

    Answer: A is probably a simple asphyxiant, such as methane, CH_4, or even elemental nitrogen, N_2. B could be a substance that prevents blood hemoglobin from binding with O_2 and could include carbon monoxide, which binds strongly to hemoglobin, or it could be a substance such as nitrite or aniline that converts hemoglobin to methemoglobin, which does not transport O_2. D would be cyanide or a substance that is metabolized to cyanide that bonds to iron(III) in iron-containing ferricytochrome oxidase enzyme, preventing the reduction of iron (III) in this enzyme to iron(II) in the oxidative phosphorylation process by which the body utilizes O_2. Since C is an antidote to cyanide poisoning, it must form methemoglobin in which the iron is iron(III), so it is likely that C is a nitrite-forming substance, such as volatile amyl nitrite which is inhaled as an antidote to cyanide poisoning.

18. Match each toxic substance from the list on the left, below, with its effect or characteristic from the list on the right and explain each choice:

(A) Methanol	(1) Inhibits acetylcholinesterase
(B) Parathion	(2) Carcinogen
(C) Phthalate esters	(3) Affects optic nerve leading to blindness
(D) Dimethylnitrosamine	(4) Very widespread

Answer: (A)-(3), (B)-(1), (C)-(4), (D)-(2)

Chapter 24
Chemical Analysis in Environmental and Toxicological Chemistry

1. A 100-mL sample of incinerator stack gas scrubber water contaminated with HCl was titrated with a 0.0500 M (moles per liter) of standard NaOH, with a volume of 15.53 mL of the NaOH required to reach the end point. What was the concentration of HCl in the scrubber water?

   Answer: Using the formula $V_{acid} \times M_{acid} = V_{base} \times M_{base}$ yields 0.0078 for the molarity of the HCl in the scrubber water.

2. Three separate analyses for ozone in the atmosphere by the formation of I_3^- ion and measurement of its absorption of light gave values of 0.133, 0.129, and 0.134 parts per million (ppm) of ozone whereas a single measurement by a chemiluminescent detector showed 0.131 ppm of ozone. What do these results imply regarding the precision and accuracy of the analyses?

   Answer: The three results of the spectrophotometric analysis of I_3^- ion are very close together indicating high precision. The mean of these three results of 0.132 ppm is very close to the value of 0.131 ppm obtained by an entirely different method using the chemiluminescent detector, which gives confidence in the accuracy of the analyses as well.

3. If you are not familiar with glassware used in volumetric quantitative analysis, look up the following three pieces of glassware used: Volumetric flask, pipet, and buret. Which of these is designed to contain a specific volume of solution, which delivers a single specified volume, and which delivers a variable volume depending upon how much of a standard solution is required to perform a titration?

   Answer: A volumetric flask contains a specific volume of solution, a pipet delivers a single specified volume, and a buret delivers an accurately measured variable volume, such as that of a titrant solution.

4. Look up the photochemical reaction that occurs when ozone is commonly measured instrumentally. What is this kind of reaction called?

   Answer: The chemiluminescent reaction $NO + O_3 \rightarrow NO_2^* + O_2$ followed by measurement of the intensity of light emitted by the excited NO_2^* species can be used to determine ozone in the atmosphere.

5. Suggest a conceptual similarity between the determination of lead by atomic absorption spectrophotometry using and the determination of carbon dioxide in air by nondispersive infrared analysis.

   Answer: In both cases the absorption of light by the analyte species is employed to measure the concentration of analyte.

6. Match each kind of substance or phenomenon actually measured as listed in the right column below with the potentially toxic substance or pollutant responsible for it from the left column.

(A) Carbon monoxide	(1) Methemoglobin
(B) Toluene	(2) Acetylcholinesterase activity
(C) Aniline	(3) Hemoglobin adduct

(D) Nerve gas 4. Hippuric acid

Answer: (A)-(3), (B)-(4), (C)-(1), (D)-2

7. The sulfur content of a unit train load of coal is to be determined to see if the fuel meets pollution standards. Suggest how a representative sample of the coal might be taken.

   Answer: This kind of analysis presents a challenge to the analytical chemist. The more samples taken means that the final sample measured would tend to be more representative, although costs and time tend to limit how many samples can be processed. A sample can be taken from each car, varying the location from which it is taken in the carload of coal randomly. Grinding and mixing all the samples taken into one composite sample to be measured should give a representative sample for analysis. Separate analyses of several of the individual samples taken from the railcars could also be done. If the values of analyte (typically sulfur) thus obtained were reasonably close together, it would provide confidence that the coal on the train was of reasonably uniform composition and that representative samples had been obtained.

8. What is the function of a hollow cathode in the atomic absorption determination of a metal? Of what kind of material is a hollow cathode composed?

   Answer: The hollow cathode lamp is the detector and the hollow cathode is composed of the same metal being determined.

9. Lead may be determined in water by using atomic absorption with both a flame atomizer and a graphite tube atomizer. Suggest how the output signal, absorbance as a function of time, would appear differently in these two modes of analysis.

   Answer: The flame atomizer should give a uniform value with time whereas the graphite tube atomizer would give a peak-shaped response, the area of which is proportional to the amount of analyte in the sample injected into the analyzer.

10. What is a titrant? How are titrants used in chemical analysis?

    Answer: A titrant is a reagent solution of known concentration. It is added to a known amount or volume of a sample to react with an analyte in the sample. In a titration procedure, the amount of titrant required to react with the analyte in the sample gives the quantity or concentration of the analyte.

11. Describe the general characteristics of a titration curve for the titration of HCl with NaOH.

    Answer: Such a titration curve is in the form of a steep "S" shape, the mid-point on the rising part of the curve corresponding to the volume of the end point of the titration.

12. How is the end point found in the titration of HCl with NaOH using either a titration curve or an indicator?

    Answer: The mid-point on the rising part of the titration curve corresponds to the volume of the end point of the titration. When an indicator is used, the volume of the titrant at which the indicator changes color corresponds to the end point.

13. A 3.471-g sample of a compound containing C, H, and O was ignited in a stream of O_2 and the CO_2 and H_2O were collected. Masses of 8.758 g of CO_2 and 1.537 g of H_2O were collected. Calculate the percentages of C and H in the compound.

    Answer:

$$\text{Mass C} = 8.758 \text{ g } CO_2 \times \frac{1 \text{ mol } CO_2}{44 \text{ g } CO_2} \times \frac{1 \text{ mol C}}{1 \text{ mol } CO_2} \times \frac{12 \text{ g C}}{1 \text{ mol C}} = 2.39 \text{ g C}$$

$$\text{Mass H} = 1.537 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18 \text{ g } H_2O} \times \frac{2 \text{ mol H}}{1 \text{ mol } H_2O} \times \frac{1 \text{ g H}}{1 \text{ mol H}} = 0.171 \text{ g H}$$

$$\text{Percent C} = \frac{2.39 \text{ g}}{3.471 \text{ g}} \times 100 = 68.9 \text{ \% C}$$

$$\text{Percent H} = \frac{0.171 \text{ g}}{3.471 \text{ g}} \times 100 = 4.93 \text{ \% H}$$

Percent O = 100 - 68.9 - 4.9 = 26.2% O

14. Based upon material covered in the chapters on atmospheric chemistry in this book and on the internet regarding the nature of electrons in atoms, quantum chemistry, and photochemistry, attempt to explain the phenomena of atomic absorption and atomic emission discussed as analytical techniques in this chapter.

    Answer: Atoms absorb light when electrons in the atoms go to higher energy levels, the basis of atomic absorption. When electrons at higher levels in atoms excited by high temperatures fall to lower energy levels, light is emitted, which is the basis of atomic emission.

15. Considering the Nernst equation as it applies to the measurement of pH, calculate the voltage change at a glass electrode used to measure pH for each unit change in pH.

    Answer: A unit change in pH corresponds to a 10-fold change in H^+ ion activity. Based upon the Nernst equation for hydrogen ion activity, Equation 24.7.4, this corresponds to a change of -59.2 millivolts for a unit increase in pH (10- fold lower H^+ ion activity) and +59.2 mv for a unit decrease in pH

16. Distinguish among the electron-capture detector, flame-ionization detector, and mass spectrometer as detectors for gas chromatographic separations.

    Answer: An electron capture detector for gas chromatography uses a beta-particle-emitting radionuclide, typically ^{63}Ni to produce electrons that are accelerated through the gas stream in the effluent from the chromatographic column. The electrical current produced is reduced by the capture of electrons by molecules that capture electrons, usually organohalide compounds, and the degree of current reduction is a measure of the concentration of the electron-capturing analyte in the chromatographic effluent. The flame ionization detector for gas chromatography detects ions formed in a flame from organic compounds, particularly hydrocarbons. With a mass spectrometric detector the mass spectra are taken of compounds separated by the chromatograph.

17. What is required to get a reasonable flow rate in a high performance liquid chromatographic separation?

    Answer: Very high pressures are required to obtain a reasonable flow rate.

18. What is the basis of separations made in mass spectrometry? Why is mass spectrometry one of the most specific means of detecting organic compounds?

    Answer: Mass spectrometry breaks molecules down into ion fragments that are separated on the basis of their mass-to-charge ratio. The masses of the fragments are measured very sensitively and the resulting mass spectrum pattern enables highly sensitive and selective measurement of the parent compound from which they were formed.

19. What are the main components of an automated analyzer system? What are the functions of each?

    Answer: The major components of such an analyzer include means of injecting sample and reagents, pump, mixing coils, and a detector, usually a colorimeter.

20. What is the basis of immunoassay analysis? What is meant by its being classified as a good screening technique?

    Answer: Immunoassay is based upon antibodies for specific compounds produced biologically. As a way of detecting analytes very specifically it is a good means of screening samples to detect compounds, which in some cases are then analyzed individually by more quantitative methods such as mass spectrometry.

21. A sample of a colored analyte at a concentration of 3.60×10^{-3} mol/L shows 34.2 percent transmittance in a 2.00 cm cell. What is the value of a in the Beer's law equation for this substance at the wavelength measured? If a sample of the colored analyte of unknown concentration gives an absorbance, A, of 0.520 in the same cell at the same wavelength, what is the concentration of the analyte in this solution?

    Answer: The absorbance, A, is given by A = log(100/%T)

    A = log(100/34.2) = 0.465 for a solution of concentration = 3.60×10^{-3} mol/L

    Solving the Beer's law equation, A = abC for the absorbance, a, gives the following:

    $a = A/bc = 0.465/(2.00 \text{ cm} \times 3.60 \times 10^{-3} \text{ mol/L}) = 64.6 \text{ L} \times \text{mol}^{-1} \times \text{cm}^{-1}$

    From the Beer's law relationship for measurements under identical conditions including cell length the concentration is directly proportional to the absorbance, A, so in this case,

    $C = (0.520/0.465) \times 3.60 \times 10^{-3} \text{ mol/L} = 4.03 \times 10^{-3} \text{ mol/L}$

22. What are the similarities between the measurement of total organic carbon (TOC) and biochemical oxygen demand (BOD) in water. What are the differences between them? Which is likely to be indicative of livestock feedlot pollution and which would suggest water pollution from industrial wastes?

    Answer: As the name implies, TOC measures the total amount of organic carbon in a water sample. BOD is a measure of the amount of oxygen consumed by the biodegradation of carbon-containing compounds and therefore essentially registers biodegradable dissolved carbon. Feedlot runoff pollution would best be analyzed by BOD and pollution from an industrial source, which may not be biodegradable, should be analyzed as TOC.

23. In a sense, the toxicity characteristic leaching procedure (TCLP) is a somewhat strange test based upon a "mismanagement scenario." What is the origin of the test and what is the mismanagement scenario?

    Answer: The TCLP test is based upon the possibility of co-disposal of toxic wastes with municipal refuse (a "waste mismanagement scenario"). "Garbage" tends to undergo biodegradation to yield materials such as acids that tend to mobilize toxic compounds into leachate from the disposal site. The TCLP test uses a weakly acidic buffer to leach toxic substances from wastes followed by the determination of likely waste constituents such as refractory organic pesticides and heavy metals.

24. Several journal articles such as Esteve-Turrillas, Francesc A., Vicent Yusa, Agustin Pastor, and Miguel de la Guardia, "The New Perspectives in the Use of Semipermeable Membrane Devices as Passive Samplers," From *Talanta*, **74**, 443-457 (2008) describe the use of semipermeable membrane devices to monitor persistent organic pollutants in the

environment. What are these devices? How are they used? Approximately when did they come into general use? What are their advantages and disadvantages?

Answer: The most common form of the semipermeable membrane device (SPMD) consists of a sealed flat segment of low density polyethylene tubing containing a thin film of a pure lipid material (triolein) that is designed to mimic lipids in fish that accumulate lipophilic pollutants such as PCBs. The devices are left in water for periods of time after which they are removed and lipophilic analytes are measured in the triolein. They have come into increasing use for monitoring water pollutants since approximately year 2000. Advantages include the ability to integrate sample over a long time period, catching transient events that might be missed by taking a single sample at one time, and relative ease of sampling.